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**CLAIMS**


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**[Claim(s)]**

[Claim 1] [A] It is the copolymer of ethylene and the alpha olefin of carbon numbers 4-20. (i) The content of the configuration unit (a) guided from ethylene 55 - 70-mol %, The content of the configuration unit (b) guided from the alpha olefin of carbon numbers 4-20 is 30 - 45-mol %. (ii) Consistencies are three or less 0.863 g/cm, and the limiting viscosity  $[\eta]$  measured in 135 (iii) degree-C decalin is 0.1 - 8.0 dl/g. (iv) The glass transition temperature measured with the differential scan mold calorimeter (DSC) is -60 degrees C or less. Degree of crystallinity is 1% or less, and it is (v). The intensity ratio ( $T^{****}/T^{****}$ ) of  $T^{****}$  to  $T^{****}$  in 13 C-NMR spectrum is 0.5 or less. (vi) The ethylene and alpha olefin [copolymer A]:99-30 % of the weight which fills the relation whose B values calculated from 13 C-NMR spectrum and the following general formula (1) are 0.9-1.5 B value =  $[POE] / (2 - [PE], [PO])$  -- (1)

(Among a formula, [PE] is the content mole fraction of the configuration unit guided from the ethylene in a copolymer, [PO] is the content mole fraction of the configuration unit guided from the alpha olefin in a copolymer, and [POE] is the rate of the ethylene and the number of alpha olefin chains to all the diad (dyad) chains in a copolymer.)

[B (a)] ethylene and the alpha olefin of the (b) carbon numbers 3-20, It is a copolymer with at least one compound chosen from the group which consists of an annular olefinic compound and an aromatic series vinyl compound. (i) A consistency is in the range of 0.890 - 0.940 g/cm<sup>3</sup>. (ii) 190 degree C, It is in the range whose melt flow rates in 2.16kg load are 0.3-50g / 10 minutes. (iii) The temperature ( $T_m$ ) and the consistency (d) of the maximum peak location in the endoergic curve measured with the differential scan mold calorimeter (DSC) The ethylene and the alpha olefin copolymer constituent characterized by consisting of ethylene system [copolymer B]:1-70 % of the weight which satisfies the relation shown by  $T_m < 400 \times d - 250$ .

[Claim 2] [A] The ethylene and the alpha olefin copolymer constituent characterized by consisting of high-density-polyethylene [C]:1-70 % of the weight which has said ethylene and alpha olefin [copolymer A]:99 - the [C (i)] consistency in the range of 0.945 - 0.970 g/cm<sup>3</sup>, and has a melt flow rate (MFR) in (ii) 190 degree C and 2.16kg load in the range for 0.3 - 50g / 10 minutes with 30 % of the weight.

[Claim 3] The resin modifier characterized by consisting of ethylene and an alpha olefin copolymer constituent according to claim 1 or 2.

[Claim 4] It is the constituent which consists of a propylene system polymer [D], said ethylene and alpha olefin copolymer [A], and an ethylene system copolymer [B]. (i) The content of a propylene system polymer [D] is [ the content (sum total of [A] and [B]) of 98 - 60 % of the weight, ethylene and an alpha olefin copolymer [A], and an ethylene system copolymer [B] ] 2 - 40 % of the weight. (ii) Propylene system polymer constituent with which the content ratio ( $[A] / [B]$ ) of ethylene and an alpha olefin copolymer [A], and an ethylene system copolymer [B] is characterized by being 99 / 1 - 30/70.

[Claim 5] It is the constituent which consists of a propylene system polymer [D], said ethylene and alpha olefin copolymer [A], and high density polyethylene [C]. (i) The content of a propylene system polymer [D] is [ the content (sum total of [A] and [C]) of 98 - 60 % of the weight, ethylene and an alpha olefin copolymer [A], and high density polyethylene [C] ] 2 - 40

% of the weight. (ii) Propylene system polymer constituent with which the content ratio ([A] / [C]) of ethylene and an alpha olefin copolymer [A], and high density polyethylene [C] is characterized by being 99 / 1 - 30/70.

[Claim 6] 190 degrees C of a propylene system polymer [D], the propylene system polymer constituent according to claim 4 or 5 characterized by the melt flow rates (MFR) in 2.16kg load being 20g / 10 minutes or more.

[Claim 7] The propylene system polymerization body composition object according to claim 4 to 6 characterized by for the peak of the damping factor resulting from the glass transition temperature of a propylene system polymer [D] and the peak of the damping factor resulting from the glass transition temperature of said ethylene and alpha olefin copolymer constituent having existed, and both peaks having dissociated when the temperature dependence of an elastic modulus is measured.

[Claim 8] The refining approach of the resin characterized by carrying out a melting blend with the resin which is going to reform the pellet which consists of ethylene and an alpha olefin copolymer constituent according to claim 1 or 2.

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[Translation done.]

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DETAILED DESCRIPTION OF THE INVENTION

[0001]

[field of the invention]

The present invention is related to useful ethylene /  $\alpha$  - olefin copolymer composition as resinous modifying agent such as polypropylene, and propylene system polymer composition including this ethylene /  $\alpha$  - olefin copolymer composition is related to.

[0002]

[a background of the invention of invention]

Technique to blend elastomer such as ethylene propylene copolymer, ethylene butene copolymer as modifying agent is well known to polypropylene resin for the purpose of improving chip resistance of polypropylene resin conventionally.

[0003]

However, there was limit in elastomeric combination quantity so that resinous stiffness properties deteriorated when elastomer was blended into polypropylene resin.

In addition, for example, there is a case to require chip resistance in cryogenic temperature as well as chip resistance with ordinary temperature in resin molded articles such as polypropylene resin molded articles.

Cryostatic temperature impulsiveness does not always accord with chip resistance with ordinary temperature, it is conceivable that soft gum is used as modifying agent to raise such a cryostatic temperature impulsiveness, but when such a judo worth gum is blended in polypropylene resin, it will fail in rigidity of compact, the above and same problem are held.

[0004]

Because of this the modifying agent which stiffness properties and balance with chip resistance can hold with a high is demanded.

On the other hand, what is not destroyed on the occasion of a service application is pursued in a resin molded article such as the above.

Because of this high stiffness properties is being maintained, and that pulling elongation at breakage is high is demanded from a resin molded article, an appearance of the resin modifying agent that in other words balance with rigidity and pulling elongation at breakage was a high was demanded.

[0005]

At Japanese Patent Laid-Open No. 6-192500 bulletin, that preferable composition of physical property balance of rigidity and chip resistance is got is disclosed by blending ethylene /  $\alpha$  - olefin copolymer having a particular property in polypropylene polymer, but it was insufficient, and, in this composition, an upgrade was demanded about balance of rigidity and cryogenic temperature bombardment hardness, rigidity and pulling elongation characteristic.

[0006]

Even more particularly, when resin property modification is done in this way, in resin modifying agent, there are feed section of kneading machine, the thing which, for example, wake up blocking in hopper at time to knead, because of this productivity turns worse, there was able to be a thing named a problem that physical property of the reforming thing which, in addition, was provided does not maintain the same.

[0007]

Thus, reforming does chip resistance in pulling elongation at breakage and cryogenic temperature in particular with having kept resinous stiffness properties such as polypropylene resin, when, besides, modifying agent is used, problems such as blocking are hard to be had, an appearance of resin modifying agent superior in productivity / working properties was desired earnestly.

[0008]

#### OBJECT OF THE INVENTION

The present invention is going to solve a problem with prior art such as the above, and reforming does resinous stiffness properties and pulling elongation at breakage in cryogenic temperature in particular and chip resistance such as polypropylene resin and when modifying agent is used, problems such as blocking are hard to be had and are in productivity, working properties for the purpose of providing superior ethylene /  $\alpha$  - olefin copolymer composition.

In addition, the present invention is for the purpose of providing a polypropylene resin composition including ethylene /  $\alpha$  - olefin copolymer composition such as the above.

[0009]

#### SUMMARY OF THE INVENTION

The first ethylene /  $\alpha$  - olefin copolymer composition concerning the present invention,

[A]

Be copolymer with  $\alpha$  - olefin of ethylene and carbon number 4-20,

(i) Content (b) of the constitutional unit that content of guided constitutional unit (a) is guided from ethylene by  $\alpha$  - olefin of 55-70 mol %, carbon number 4-20 is 30-45 mol %,

(ii) Apparent density of board is equal to or less than 0.863g/cm<sup>3</sup>,

(iii) Limiting viscosity  $[\eta]$  measured in 135 degrees Celsius decalin is 0.1-8.0dl/g,

(iv) Glass transformation temperature measured at differential scanning type calorimeter (DSC) is equal to or less than -60 degrees Celsius, and crystallinity is less than 1%,

(v) Intensity ratio ( $T_{\alpha\beta} / T_{\alpha\alpha}$ ) of  $T_{\alpha\beta}$  as opposed to  $T_{\alpha\alpha}$  in a <sup>13</sup>C - NMR spectrum is equal to or less than 0.5,

(vi) <sup>13</sup>C - NMR spectrum and ethylene /  $\alpha$  - olefin copolymer [A] which satisfy the relationship that is 0.9-1.5 found B value from the following regular expression (1), 99-30 % by weight:

$$B \text{ value} = [POE] / (2. [PE], [PO]) \dots (1)$$

([PE] is component mole fraction of a constitutional unit guided by ethylene in copolymer, and [PO] is component mole fraction of a constitutional unit guided by  $\alpha$  - olefin of the whole copolymer, and, in an expression, there is [POE] at the rate of ethylene /  $\alpha$  - olefin linkage number for all dyad (dyad) linkage of the whole copolymer.)

[B]

(a) Ethylene,

(b) It is copolymer with at least one chemical agent chosen by group comprising  $\alpha$  - olefin of carbon number 3-20, a cyclic olefin system compound and aromatic vinyl compound and,

(i) There is apparent density of board in a range of 0.890-0.940g/cm<sup>3</sup>,

(ii) There are 190 degrees Celsius, melt flow rate in 2.16kg load in a range for 0.3-50g /10,

(iii) Ethylene system copolymer [B] satisfying the relationship that temperature ( $T_m$ ) and density (d) of a maximum peak location in endotherm curve measured in differential scanning type calorimeter (DSC) are shown to in  $<400 \times T_m d - 250$  is characterized by it being from 1-70 % by weight.

[0010]

The second ethylene /  $\alpha$  - olefin copolymer composition concerning the present invention,

[A]

Ethylene /  $\alpha$  - olefin copolymer [A], 99-30 % by weight:

[C]

- (i) There is apparent density of board in a range of 0.945-0.970g/cm<sup>3</sup>.
- (ii) High density polyethylene [C] in a range for 0.3-50g/10 is characterized by it being from 1-70 % by weight 190 degrees Celsius, melt flow rate (MFR) in 2.16kg load.

[0011]

Ethylene /  $\alpha$  - olefin copolymer composition such as the above is useful as resin modifying agent.

The first propylene system polymer composition concerning the present invention is propylene system polymer [D] and the composition that it is from ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B] and,

- (i) Total) of [B] that content 98-60 of propylene system polymer [D] invite content ([A] of % by weight, ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B] is 2-40 % by weight,
- (ii) It is characteristic of that content ratio ([A] / [B]) with ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B] is 99/1-30/70.

[0012]

The second propylene system polymer composition concerning the present invention is propylene system polymer [D] and the composition that it is from ethylene /  $\alpha$  - olefin copolymer [A] and high density polyethylene [C] and,

- (i) Total) of [C] that content 98-60 of propylene system polymer [D] invite content ([A] of % by weight, ethylene /  $\alpha$  - olefin copolymer [A] and high density polyethylene [C] is 2-40 % by weight,
- (ii) It is characteristic of content ratio ([A] / [C]) with ethylene /  $\alpha$  - olefin copolymer [A] and high density polyethylene [C] that it is 99/1-30/70.

[0013]

It is preferable for that to be all for 190 degrees Celsius of propylene system polymer [D], melt flow rate (MFR) in 2.16kg load for 20g/10.

In addition, when the propylene system polymer composition measured temperature dependency of degree of elasticity, preferred there is peak of an attenuation factor due to glass transformation temperature of peak of an attenuation factor due to glass

transformation temperature of propylene system polymer [D] and the ethylene /  $\alpha$  - olefin copolymer composition and both peak separating.

[0014]

A resinous property modification method concerning the present invention is characterized by resin and the melt blended which are going to do reforming doing a pellet comprising the ethylene /  $\alpha$  - olefin copolymer composition of the first or the second.

[0015]

#### DETAILED DESCRIPTION OF THE INVENTION

The following, ethylene /  $\alpha$  - olefin copolymer composition concerning the present invention and the use will be explained concretely.

[0016]

At first the first ethylene /  $\alpha$  - olefin copolymer composition explains the first ethylene /  $\alpha$  - olefin copolymer concerning the present invention.

[0017]

Preferably preferably, as for the first ethylene /  $\alpha$  - olefin copolymer composition concerning the present invention, it is from 10-50 % by weight 1-70 % by weight 90-50 % by weight and ethylene system copolymer [B] 99-30 % by weight ethylene /  $\alpha$  - olefin copolymer [A].

In addition, (100 with ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B] in total is % by weight.)

Ethylene /  $\alpha$  - olefin copolymer [A]

Ethylene /  $\alpha$  - olefin copolymer [A] used with the present invention is copolymer with  $\alpha$  - olefin of ethylene and carbon number 4-20.

[0018]

For  $\alpha$  - olefin of this carbon number 4-20, one - butene, one - pentene, one - hexene, three - carbonyl -1 - butene, three - carbonyl -1 - pentene, three - ethyl -1 - pentene, four - carbonyl -1 - pentene, four - carbonyl -1 - hexene, 4, 4- dimethyl -1 - pentene, four one - ethyl -1 - hexene - octene, three - ethyl -1 - hexene, one - octene, one - decene, one - dodecen, one - tetradecene, one - hexadecene, one - octadecene, one - eicosen are given to be concrete.

Of these, it is preferable, and one - butene, one - hexene, one - octene are used.

(i) Preferably preferably 30-45 mol %, is 40-30 mol % content of constitutional unit

(b) guided by  $\alpha$  - olefin of 60-70 mol %, carbon number 4-20 55-70 mol %, content of constitutional unit (a) which ethylene /  $\alpha$  - olefin copolymer [A] used with the content present invention of each constitutional unit in ethylene /  $\alpha$  - olefin

copolymer [A] is guided to by ethylene.

(ii) Apparent density of board is lower than 0.863g/cm<sup>3</sup>, and preferably there is ethylene /  $\alpha$  - olefin copolymer [A] used with the apparent density of board present invention in field of 0.855-0.860g/cm<sup>3</sup>.

(iii) 0.1-8.0dl/g are desirable, and 1-5dl/g depend, and preferably, as for ethylene /  $\alpha$  - olefin copolymer [A] used with the limiting viscosity present invention, there is limiting viscosity  $[\eta]$  measured in 135 degrees Celsius, decalin in field of 2-5dl/g.

(iv) Lower than -60 degrees Celsius are desirable, and the glass transformation temperature that ethylene /  $\alpha$  - olefin copolymer [A] used with glass transformation temperature and the crystallinity present invention measured in differential scanning type calorimeter (DSC) is lower than -65 degrees Celsius, and lower than 1% are desirable, and crystallinity is lower than 0.5%.

(v) Preferably lower than 0.2 depend, and preferably, as for ethylene /  $\alpha$  - olefin copolymer [A] used with the  $T_{\alpha\beta}/T_{\alpha\alpha}$  present invention, lower than 0.5 are under 0.01 intensity ratio ( $T_{\alpha\beta}/T_{\alpha\alpha}$ ) of  $T_{\alpha\beta}$  for  $T_{\alpha\alpha}$  in <sup>13</sup>C - NMR spectra.

[0019]

$T_{\alpha\alpha}$  in a <sup>13</sup>C - NMR spectrum and  $T_{\alpha\beta}$  are peak intensity of CH<sub>2</sub> of the whole constitutional unit guided by  $\alpha$  - olefin of more than carbon number 4 here, and location for the third grade carbon means two kinds of different CH<sub>2</sub> as shown in follows.

[0020]

[CHEMICAL FORMULA1]

[0021]

Such a  $T_{\alpha\beta}/T_{\alpha\alpha}$  intensity ratio is done as follows, and it can request. For example, JEOL-GX270NMR measuring apparatus made in JEOL Ltd. is used, and a <sup>13</sup>C - NMR spectrum of ethylene /  $\alpha$  - olefin copolymer [A] is measured.

Measurement uses mixed solution of hexachlorobutadiene / d<sub>6</sub>- benzene =2/1 (volume ratio) that is adjusted to become five sample density % by weight, and it is performed in 67.8MHz, 25 degrees Celsius, d<sub>6</sub>- benzene (128ppm) standard.

A measured <sup>13</sup>C - NMR spectrum is analyzed according to proposal (Analysis Chemistry43, p1245(1971)) of Linde man Adams, J.C.Randall (Review Macromolecular Chemistry Physics, C29, 201 (1989)), and  $T_{\alpha\beta}/T_{\alpha\alpha}$  intensity ratio is demanded.

(vi) 0.9-1.5 are desirable, and the B value that <sup>13</sup>C - NMR spectra amounts to ethylene /  $\alpha$  - olefin copolymer [A] used with the B value present invention, and is demanded



by follows general formula (1) is 1.0-1.2.

[0022]

B value = [ POE ] / ( 2. [ PE ], [ PO ] ) ... (1)

([PE] is component mole fraction of a constitutional unit guided by ethylene in copolymer, and [PO] is component mole fraction of a constitutional unit guided by  $\alpha$  - olefin of the whole copolymer, and, in an expression, there is [POE] at the rate of ethylene /  $\alpha$  - olefin linkage number for all dyad (dyad) linkage of the whole copolymer.)

This B value is indicator presenting distribution condition with  $\alpha$  - olefin of ethylene and carbon number 4-20 in ethylene /  $\alpha$  - olefin copolymer [A], and J. C. Randall (Macromolecules, 15, 353 (1982)), a report of J. Ray (Macromolecules, 10, 773 (1977)) are based on, and it can be demanded.

[0023]

Block linkage of ethylene or  $\alpha$  - olefin copolymer shortens so that B value is big, distribution of ethylene and  $\alpha$  - olefin is the same, and that component cloth of copolymerization gum is small is shown.

In addition, component cloth of ethylene /  $\alpha$  - olefin copolymer becomes wide, and there is bad point that the handling characteristics turn worse so that B value shrinks than 1.0.

[0024]

As for production method such ethylene /  $\alpha$  - olefin copolymer [A] of ethylene /  $\alpha$  - olefin copolymer [A], an existence bottom of metallocene system catalyst can produce  $\alpha$  - olefin of ethylene and carbon number 4-20 by making do copolymerization.

[0025]

Such a metallocene system catalytic substance may be formed by metallocene compound (a) and organoaluminum hydroxy- compound (b) and metallocene compound (a) and chemical agent (c) which it is responded, and form ion pair, even more particularly, may be formed with (a), (b) and (c) by organoaluminum compound (d).

[0026]

Each these ingredients are explained below.

(a)

Metallocene chemical agent (a) forming a metallocene system catalytic substance used with the metallocene compound present invention is metallocene chemical agent of transition metal chosen by 周期律表第 IVB family, and it is presented in follows general formula (2) concretely.

[0027]

MLx ... (2)

In [regular expression (2), transition metal, x that M is chosen among 周期律表 第 IVB group are.] that valency of transition metal M, L are ligand

In regular expression (2), Zr, titanium and hafnium are given for the person that transition metal shown to in M is concrete.

[0028]

In regular expression (2), L is ligand doing coordination in transition metal, and ligand L of one is ligand having a cyclopentadienyl skeleton among these at least. Ligand having this cyclopentadienyl skeleton may have substituent.

Cyclopentadienyl group, for example, to substitute for cyclopentadienyl group, carbinyl cyclopentadienyl group, ethyl cyclopentadienyl group, n- or i- propyl cyclopentadienyl group, n-, i-, sec-, t-, butyl cyclopentadienyl group, dimethyl cyclopentadienyl group, methylpropyl cyclopentadienyl group, methylbutyl cyclopentadienyl group, alkyl such as methylbenzyl cyclopentadienyl group or cycloalkyl for ligand L having a cyclopentadienyl skeleton.

Even more particularly, the indenyl basis, 4,5,6,7- tetrahydro indenyl bases, the fluorenyl basis are put up.

[0029]

The basis having the cyclopentadienyl skeleton may be substituted for in halogen atom or trialkylsilyl group.

When a compound presented in regular expression, (2) has the basis having a cyclopentadienyl skeleton more than two as ligand L, soon, radical having two cyclopentadienyl skeletons, alkylene group such as ethylene, propylene,

Permutation alkylene group such as isopropylidene, diphenylmethylenes,

Permutation buttocs Ren radical such as the buttocs Ren basis or the dimethylsilylene basis, the diphenyl buttocs Ren basis, the methylphenyl buttocs Ren basis is gone through, and it may be coupled.

[0030]

For ligand (the ligand which does not have a cyclopentadienyl skeleton) L except ligand having a cyclopentadienyl skeleton, hydrocarbon group of carbon number 1-12, alkoxy group, the aryloxy basis, sulfonic acid component radical (-SO<sub>3</sub>Ra), halogen atom or hydrogen atom (here, Ra is aryl substituted for in an alkyl group, an alkyl group, aryl substituted for in halogen atom or halogen atom or alkyl group.) is given.

[0031]

An alkyl group, cycloalkyl groups, aryl and aralkyl group are nominated for hydrocarbon group of carbon number 1-12.

Alkyl group such as dodecyl group, methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, t-butyl group, pentyl group, a hexyl group, octyl radical, decyl for concreteness.

Cycloalkyl groups such as cyclopentyl group, cyclohexyl group,

Aryl such as phenyl group, tolyl group,

Aralkyl group such as benzyl group, the neophyl basis is given.

[0032]

Methoxy group, ethoxy group, a n-propoxy group are nominated for alkoxy group.

Phenoxy group is nominated for the aryloxy basis.

For the sulfonic acid component basis ( $-SO_3Ra$ ), the methane sulfonato basis, the p-toluene sulfonato basis, the trifluoromethanesulfonato basis, the p-chlorobenzene sulfonato basis are given.

Fluorine, Cl, bromine, iodine are nominated for halogen atom.

[0033]

When, for example, as for the metallocene compound presented by the regular expression (2), valency of transition metal is 4, it stops, and is presented in follows general formula (3) concretely.

$R_2kR_3lR_4mR_5nM \dots$  (3)

M is transition metal of regular expression (2), and  $R_3$  that  $R_2$  is the basis having a cyclopentadienyl skeleton (ligand),  $R_4$  and  $R_5$  are independent respectively, and, in [regular expression (3)], a cyclopentadienyl skeleton is had, or it is the radical which is not had (ligand).

.] that  $k + l + m + n = 4$

For such metallocene compound (a), screw (cyclopentadienyl) Zr dichloride, screw (methylcyclopentadienyl) Zr dichloride, screw (ethyl cyclopentadienyl) Zr dichloride, screw (n-propyl cyclopentadienyl) Zr dichloride, bis (n-butylcyclopentadienyl) Zr dichloride, bis (n-hexyl cyclopentadienyl) Zr dichloride, bis (carbinyl -n-propyl cyclopentadienyl) Zr dichloride, bis (carbinyl -n-butylcyclopentadienyl) Zr dichloride,

Screw (dimethyl -n-butylcyclopentadienyl) Zr dichloride, screw (n-butylcyclopentadienyl) Zr dibromide, screw (n-butylcyclopentadienyl) Zr methoxy chloride, screw (n-butylcyclopentadienyl) Zr ethoxy chloride, screw (n-butylcyclopentadienyl) Zr butoxy chloride, bis (n-butylcyclopentadienyl) Zr ethoxide, bis (n-butylcyclopentadienyl) Zr methyl chloride, bis (n-butylcyclopentadienyl) ジルコニ It is given ウムジメチル, screw (n-butylcyclopentadienyl) Zr benzyl chloride, screw (n-butylcyclopentadienyl) Zr

dibenzyl, screw (n-butylcyclopentadienyl) Zr phenyl chloride, screw (n-butylcyclopentadienyl) Zr hydride chloride, などが.

In addition, in the illustration, as for disubstituted body 1, 2- of cyclopentadienyl ring and 1, 3- substitution product are included.

In addition, with the present invention, metallocene chemical agent (a) which replaced Zr metal with titanium metal or hafnium metal can be used in zirconium compound such as the above.

[0034]

Even more particularly, at least 2, metallocene chemical agent of this bridge type that, at a minimum, two radical goes through alkylene group, substitution alkylene group, buttocks Ren radical or substitution buttocks Ren radical, and is coupled that, for example, R2 and R3 are radical having a cyclopentadienyl skeleton (ligand) of R2 of the regular expression (3) inside, R3, R4 and R5 can be used as metallocene compound (a).

It is similar to ligand L except R4 and ligand having the cyclopentadienyl skeleton that R5 was explained of regular expression (2) for independency respectively then.

[0035]

For metallocene compound (a) of such a bridge type, metallocene chemical agent as claimed in Japanese Patent Laid-Open No. 4-268307 presented in ethylenebis (indenyl) dimethyl Zr, ethylenebis (indenyl) Zr dichloride, isopropylidene (cyclopentadienyl - fluorenyl) Zr dichloride, diphenyl buttocks Ren bis (indenyl) Zr dichloride, methylphenyl buttocks Ren bis (indenyl) Zr dichloride and follows general formula (4) is given.

[0036]

[CHEMICAL FORMULA2]

[0037]

M1 is metal of 第 IVB group of periodic table, and, in the regular expression (4), titanium, Zr, hafnium are given concretely.

In addition, in the regular expression (4), R1 and R2 may be different each other in the same, for concreteness, hydrogen atom,

Carbon number 1-10, it is preferable, 1-3 alkyl groups,

Carbon number 1-10, it is preferable, 1-3 alkoxy group,

Carbon number 6-10, it is preferable, 6-8 aryl,

Carbon number 6-10, it is preferable, 6-8 aryl oxy group,

Carbon number 2-10, it is preferable, 2-4 alkenyl group,

Carbon number 7-40, it is preferable, 7-10 arylalkyl group,

Carbon number 7-40, it is preferable, 7-12 alkyl aryl,  
Carbon number 8-40, it is preferable, 8-12 aryl alkenyl group,  
Or preferably halogen atom is chlorine atom.

[0038]

In a more regular expression (4), R3 and R4, hydrogen atom,  
Halogen atom is preferable, fluorine atom, chlorine atom or bromine atom,  
Carbon number 1-10 which may be halogenated, it is preferable, 1-4 alkyl groups,  
Carbon number 6-10, it is preferable, 6-8 aryl,  
It is -N (R10) 2, -SR10, -OSi(R10) 3, -Si(R10) 3 or two -P(R10).  
As for R10, halogen atom is preferable, chlorine atom,  
Carbon number 1-10, it is preferable, 1-3 alkyl groups,  
Or carbon number 6-10 are preferable, and it is 6-8 aryl.  
R3 and R4 may be different each other in the same, and it is preferable to be hydrogen atom in particular.

[0039]

In the regular expression (4), as for R5 and R6, R3 and a thing same as radical exemplified in R4 are given except hydrogen atom.

It may be different each other in the same, and preferably R5 and R6 are the same.  
An alkyl group of carbon number 1-4 or a halogenation alkyl group is preferable, and it appears, and, for R5 and R6, there is, it is methyl group, ethyl group, propyl group, isopropyl group, butyl group and isobutyl group or trifluoromethyl group concretely, and methyl group is particularly desirable.

[0040]

In regular expression (4), R7

[0041]

[CHEMICAL FORMULA3]

[0042]

It is =BR11, =AIR11, -Ge-, -Sn-, -O-, -S-, =SO, =SO2, =NR11, =CO, =PR11 or =P(O)R11.

R11, R12 and R13, hydrogen atom,

Halogen atom,

Preferably, carbon number 1-10, it is preferable 1-4 alkyl groups, methyl group,  
A fluoroalkyl group of carbon number 1-10 is preferable, the CF3 basis,  
Carbon number 6-10, it is preferable, 6-8 aryl,  
Fluoroaryl of carbon number 6-10 is preferable, pentafluoro phenyl group,  
Preferably, carbon number 1-10, it is particularly preferable 1-4 alkoxy group,

methoxy group,

Carbon number 2-10, it is preferable, 2-4 alkenyl group,

Carbon number 7-40, it is preferable, 7-10 arylalkyl group,

Carbon number 8-40, it is preferable, 8-12 aryl alkenyl group,

Or carbon number 7-40 are preferable, and it is 7-12 alkyl aryl.

'R11 and R12' or 'R11 and R13' are become with the atom which they couple respectively, and ring may be formed.

R11, R12 and R13 may be different each other in the same.

[0043]

Silicon, germanium or tin is preferable, and the M2 is silicon or germanium.

It is preferable for R7 to be, = CR11R12, = SiR11R12, = GeR11R12, -O-, -S-, = SO, = PR11 or = P (O) R11.

[0044]

In regular expression (4), it is R11 and  $\text{じものがあげれらる}$  for R8 and R9.

R8 and R9 are the same each other and may be different.

Zero, 1 or 2 are preferable respectively, and, in regular expression (4), m and n are zero or 1, and preferably m+n zero, 1 or 2 are zero or 1.

m and n are the same each other and may be different.

[0045]

Two rac- ethylene (two - carbonyl -1 - indenyl) - Zr - dichloride, two rac-dimethylsilylene (two - carbonyl -1 - indenyl) - Zr - dichloride are nominated for metallocene compound (a) presented by regular expression (3).

[0046]

Metallocene compound (a) presented by such a regular expression (3) can be produced by a well-known method (for example, Japanese Patent Laid-Open No. 4-268307 bulletin is referred to).

In addition, metallocene chemical agent presented by the following regular expression (5) as metallocene compound (a) presented by regular expression (3) can be used.

[0047]

[CHEMICAL FORMULA4]

[0048]

In regular expression (5), M shows transition metal atom of 周期律表第 IVB group, it is titanium, Zr, hafnium to be concrete.

In regular expression (5), R1 and R2 show hydrogen atom, halogen atom, hydrocarbon group of carbon number 1-20, halogenation hydrocarbon group of carbon number 1-20,

silicon component radical, oxygen component radical, sulfur component radical, nitrogen component radical or phosphorus component radical to independency respectively, for concreteness, halogen atom such as fluorine, Cl, bromine, iodine,

Hydrocarbon group of carbon number 1-20 such as aryl such as carbinyl, ethyl, propyl, butyl, hexyl, cyclohexyl, octyl, nonyl, dodecyl, an Aiko sill, norbornyl, alkyl group such as adamanthyl, vinyl, propenyl, alkenyl group such as cyclohexenyl, benzil, phenylethyl, arylalkyl group such as phenylpropyl, phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propyl phenyl, biphenyl, naphthyl, carbinyl naphthyl, アントラセニル, phenanthryl,

Halogenation hydrocarbon group of carbon number 1-20 which halogen atom substituted the hydrocarbon group for,

Methylsilyl, thing carbon hydride permutation silyl such as phenyl Cyril, dimethylsilyl, dihydrocarbon substitution silyl such as diphenyl silyl, trimethylsilyl, triethylsilyl, tripropyl silyl, tricyclo hexyl silyl, triphenylsilyl, dimethylphenylsilyl, carbinyl diphenyl silyl, tritoyl silyl, trihydrocarbon substitution silyl such as trinaphthyl silyl, silyl ether of hydrocarbon substitution silyl such as trimethylsilyl ether, silicon substitution alkyl group such as trimethylsilylmethyl, silicon substitution aryl such as trimethylsilyl phenyl, などの silicon component radical,

Oxygen component radical such as aryl alkoxy group such as the hydroxy basis, methoxy, ethoxy, propoxy, alkoxy group such as butoxy, phenoxy, methylphenoxy, dimethylphenoxy, the アリロ - Kishi bases such as naphthoxy, phenylmethoxy, phenyl ethoxy,

The sulfur component bases such as the substituent which oxygen of the oxygen component basis substituted sulfur for,

Nitrogen component radical such as amino group, methylamino, dimethylamino, diethylamino, dipropylamino, dibutylamino, alkylamino groups such as dicyclohexyl amino, phenylamino, diphenylamino, ditolylamino, dinaphthyl amino, arylamino radical such as methylphenyl amino or alkyl arylamino radical,

The Lin component bases such as the Foss fino bases such as dimethyl Foss fino, diphenyl Foss fino are given.

[0049]

Of these, hydrocarbon group is preferable, and an alkyl group of carbon number 1-3 of carbinyl in particular, ethyl or propyl is preferable.

It is independent respectively, and R3, R4, R5 and R6 are the halogenated hydrocarbon bases of hydrogen atom, halogen atom, hydrocarbon group of carbon number 1-20 or

carbon number 1-20.

As for these, R1 and a person same as R2 are arrested.

Of these, it is preferable to be hydrogen, hydrocarbon group or the halogenated hydrocarbon basis.

[0050]

In addition, aromatic ring of monocycle at least one set couples among R3 and R4, R4 and R5, R5 and R6 each other, and to form may be formed, a thing presented in follows general formula (6) - (8) for ligand including aromatic ring is given.

[0051]

[CHEMICAL FORMULA5]

[0052]

When there is hydrocarbon group or halogenated hydrocarbon radical more than two kinds among R3, R4, R5 and R6 (as for the basis except the basis to form aromatic ring), these couple each other, and metallocene compound (a) presented by such a regular expression (5) may become ringed.

In addition, when R6 is substituent except aromatic group, it is preferable to be hydrogen atom.

[0053]

In regular expression (5), X1 and X2 show hydrogen atom, halogen atom, hydrocarbon group of carbon number 1-20, halogenation hydrocarbon group of carbon number 1-20, oxygen component radical or sulfur component radical to independency respectively.

[0054]

For halogen atom, hydrocarbon group of carbon number 1-20, halogenation hydrocarbon group of carbon number 1-20, the person that the oxygen component basis is concrete, R1 and a thing same as R2 can be exemplified.

[0055]

In addition, for the sulfur component basis, スルフィネート radical such as R1, basis same as R2 and carbonyl sulfonate, トリフルオロメタンスルフォネート, フェニルスルフォネート, ベンジルスルフォネート, p-トルエンスルフォネート, トリメチルベンゼンスルフォネート, トリイソブチルベンゼンスルフォネート, p-クロルベンゼンスルフォネート, スルフォネート radical such as ペンタフルオロベンゼンスルフォネート, メチルスルフィネート, フェニルスルフィネート, ベンゼンスルフィネート, p-トルエンスルフィネート, トリメチルベンゼンスルフィネート, ペンタフルオロベンゼンスルフィネート is given.

[0056]

In regular expression (5), hydrocarbon group of 2 values of carbon number 1-20,



halogenation hydrocarbon group of 2 values of carbon number 1-20, silicon component radical of 2 values, germanium component radical of 2 values, tin component radical of 2 values, -O-, -CO-, -S-, -SO-, -SO<sub>2</sub>-, -NR<sub>7</sub>-, -P(R<sub>7</sub>)-, -P(O) show -, -BR<sub>7</sub>- or -AlR<sub>7</sub>- (but, R<sub>7</sub>, hydrogen atom, halogen atom, hydrocarbon group of carbon number 1-20, halogenated hydrocarbon basis of carbon number 1-20) to Y(R<sub>7</sub>).

.] that [R<sub>7</sub> is R<sub>1</sub>, halogen atom same as R<sub>2</sub>, hydrocarbon group of carbon number 1-20, the halogenated hydrocarbon basis of carbon number 1-20

Hydrocarbon group of 2 values of and, for such Y, it is concrete carbon number 1-20 such as aryl alkylene group such as methylene, dimethyl methylene, 1,2- ethylene, 1,2- dimethyl - ethylene, 1,3- trimethylene, 1,4- tetramethylene, 1,2- cyclohexylene, alkylene group such as 1,4- cyclohexylene, diphenylmethylene, 1,2- diphenyl - ethylene,

The halogenation hydrocarbon group which halogenated hydrocarbon group of 2 values of carbon number 1-20 such as chloromethylene,

Silicon component radical of 2 values such as methylsilylene, dimethylsilylene, diethyl buttocks Ren, di(n- propyl) buttocks Ren, di(i- propyl) buttocks Ren, di(cyclohexyl) buttocks Ren, methylphenyl buttocks Ren, diphenyl buttocks Ren, di(p- tolyl) buttocks Ren, alkyl buttocks Ren of di(p- chlorophenyl) buttocks Ren, alkyl aryl buttocks Ren, aryl buttocks Ren radical, tetramethyl - 1,2- dibuttocks Ren, alkyl dibuttocks Ren of tetraphenyl - 1,2- dibuttocks Ren, alkyl aryl dibuttocks Ren, aryl dibuttocks Ren radical,

The germanium component basis of 2 values that substituted germanium for silicon of the silicon component basis of 2 values,

Tin component basis substituent of 2 values that substituted tin for silicon of the silicon component basis of 2 values is given.

[0057]

Of these, it is desirable to be the silicon component basis of 2 values, the germanium component basis of 2 values, the tin component basis of 2 values, and, even more particularly, silicon component radical of 2 values is desirable, and alkyl buttocks Ren radical, alkyl aryl buttocks Ren radical, aryl buttocks Ren radical are particularly desirable.

[0058]

In a compound presented by such a regular expression (5), it is desirable R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and that two radical including R<sub>3</sub> is alkyl group of carbon number 1-20 among R<sub>6</sub>, and it is desirable that R<sub>3</sub> and R<sub>5</sub> or R<sub>3</sub> and R<sub>6</sub> are alkyl group particularly.

It is preferable for this alkyl group to be the second grade or the third grade alkyl

group, and such an alkyl group may be substituted for in halogen atom, the silicon component basis.

Substituent exemplified in R1, R2 is nominated for halogen atom, the silicon component basis.

Even more particularly, it is preferable R3, R4, R5 and for the basis except an alkyl group to be hydrogen atom in R6.

For an alkyl group of carbon number 1-20, methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, tert-butyl group, pentyl group, a hexyl group, cyclohexyl group, heptyl radical, octyl radical, nonyl radical, dodecyl group, Aiko sill radical, norbornyl radical, chain alkyl group such as adamantyl radical and cyclic alkyl group,

Arylalkyl group such as benzyl group, phenyl ethyl group, the フェニルプロピル basis, tolyl methyl group is given, double bond, a triple association may be included.

In addition, two kinds of bases chosen among these couple R3, R4, R5 and R6 each other, and monocycle except aromatic ring or polycyclic may be formed.

[0059]

rac-dimethylsilylene - screw (4,7-dimethyl -1 - indenyl) Zr dichloride, rac-dimethylsilylene - screw (2,4,7-trimethyl -1 - indenyl) Zr dichloride, rac-dimethylsilylene - screw (2,4,6-trimethyl -1 - indenyl) Zr dichloride are nominated for such metallocene compound (a) to be concrete.

[0060]

Metallocene chemical agent (a) which substituted titanium metal, hafnium metal for Zr metal in a compound such as the above can be used.

Metallocene compound (a) is used as normal racemic body, but R type or S type can be used.

[0061]

In addition, preferred, R3 can use metallocene chemical agent (a) which is aryl of carbon number 6-16 such as phenyl group,  $\alpha$ -naphthyl group,  $\beta$ -naphthyl group, アントラセニル radical, phenanthryl-group, pyrenyl radical, Ase naphthyl group, phenalenyl radical (the ペリナフテニル basis), アセアントリレニル radical as metallocene compound (a) presented by regular expression (5).

These aryl may be substituted for in the halogenated hydrocarbon basis of halogen atom same as R1, hydrocarbon group of carbon number 1-20 or carbon number 1-20.

Of these, phenyl group in particular, naphthyl group are preferable.

[0062]

As such a metallocene compound, rac-dimethylsilylene - screw (four - phenyl -1 -

indenyl) Zr dichloride, rac- dimethylsilylene - screw (two - carbonyl -4 - phenyl -1 - indenyl) Zr dichloride, rac- dimethylsilylene - screw (two - carbonyl -4 - ( $\alpha$  - naphthyl) -1 - indenyl) Zr dichloride, rac- dimethylsilylene - screw (two - carbonyl -4 - ( $\beta$  - naphthyl) -1 - indenyl) Zr dichloride, rac- dimethylsilylene - bis (two one one - carbonyl -4 - (- アントラセニル) - - indenyl) Zr dichloride are given to be concrete.

[0063]

In addition, the transition metal compound which replaced Zr metal with titanium metal or hafnium metal can be used in above compounds.

In addition, transition metal compound presented by the following regular expression (9) can be used.

[0064]

[CHEMICAL FORMULA6]

[0065]

In the expression, M is transition metal atom of 周期律表第 IVB group, and it is titanium, Zr or hafnium, and preferably it is Zr to be concrete.

R1 is same each other, and it may be different, and number of carbon atom is next among radical or 12-40 arylalkyl group, aryl alkenyl group of number of carbon atom 13-40, number of carbon atom are 12-40 alkyl aryl or silicon component radical or 11-20 aryl, number of carbon atom are shown to in R1 higher than nothing at least soon, at a minimum, two radical forms one or more aromatic ring or aliphatic ring with the carbon atom which they couple.

For this case, ring formed by R1 includes the carbon atom which R1 couples, and, as a whole, number of carbon atom is 4-20.

[0066]

The phenyl group which at least two bases to be adjacent among the bases shown in R1 condensed for the example which formed one or more aromatic ring or aliphatic ring with the carbon atom which they couple, the cyclohexyl group which it condensed, the cyclopentadienyl group which it condensed, the dihydro cyclopentadienyl group which it condensed, the indenyl radical which it condensed, the tetrahydro indenyl which it condensed, the fluorenyl radical which it condensed, the tetrahydro fluorenyl radical which it condensed, the octahydro fluorenyl radical which it condensed are given.

In addition, these bases may be substituted for in a chain alkyl group, a ringed alkyl group, halogen atom, a halogenation alkyl group, aryl, silicon component radical, oxygen component radical, nitrogen component radical or phosphorus

component radical.

[0067]

R1 except aryl, arylalkyl group, aryl alkenyl group, alkyl aryl and R1 forming aromatic ring, an aliphatic loop is the radical that hydrogen atom, halogen atom, number of carbon atom contain 1-10 alkyl group or silicon.

[0068]

Biphenyl, anthryl, phenanthryl are nominated for 11-20 aryl number of carbon atom, phenanthryl carbonyl, phenanthryl ethyl, phenanthryl propyl are given for 12-40 arylalkyl group number of carbon atom, for aryl alkenyl group of number of carbon atom 13-40, vinyl phenanthryl is given, carbonyl phenanthryl, ethyl phenanthryl, propyl phenanthryl are given for 12-40 alkyl aryl number of carbon atom, for halogen atom, fluorine, Cl, bromine, iodine are given, carbonyl, ethyl, propyl, butyl, hexyl, cyclohexyl, octyl, nonyl are 挙げらる for 1-10 alkyl group number of carbon atom.

[0069]

For the silicon component basis, radical such as methylsilyl, phenyl silyl, dimethylsilyl, diethyl silyl, diphenyl silyl, trimethylsilyl, triethylsilyl, tripropyl silyl, tricyclohexyl silyl, triphenylsilyl, dimethylphenylsilyl, carbonyl diphenyl silyl, tritolyl silyl, trinaphthyl silyl is given.

[0070]

In addition, Halogen may substitute for an alkyl group such as the above, aryl, arylalkyl group, aryl alkenyl group, alkyl aryl.

R2 is same each other and may be different, and 7-40 arylalkyl group, aryl alkenyl group of number of carbon atom 8-40, number of carbon atom are 7-40 alkyl aryl, silicon component radical, oxygen component radical, sulfur component radical, nitrogen component radical or phosphorus component radical 2-10 alkenyl group, number of carbon atom 6-20 aryl, number of carbon atom 1-10 alkyl groups, number of carbon atom hydrogen atom, halogen atom, number of carbon atom.

[0071]

In addition, at least two bases to be adjacent among the bases shown to in R2 may form one or more aromatic ring or aliphatic ring with the carbon atom which they couple.

For this case, ring formed by R2 includes the carbon atom which R2 couples, and, as a whole, number of carbon atom is 4-20, and R2 except R2 forming aromatic ring, aliphatic ring is the radical that hydrogen atom, halogen atom, number of carbon atom contain 1-10 alkyl group or silicon.

[0072]

In addition, the embodiment that it is included by the configuration that fluorenyl radical seems to be follows in the radical which two bases shown to in R2 form one or more aromatic ring or aliphatic ring, and is constructed as.

[0073]

[CHEMICAL FORMULA7]

[0074]

Number of carbon atom can exemplify the basis same as the above and an atom for 1-10 alkyl groups and halogen atom.

Phenyl, biphenyl,  $\alpha$  - or  $\beta$  - naphthyl, anthryl, phenanthryl are given for 6-20 aryl number of carbon atom, benzil, phenylethyl, phenylpropyl, phenanthryl carbinyl, phenanthryl ethyl, phenanthryl propyl are given for 7-40 arylalkyl group number of carbon atom, for aryl alkenyl group of number of carbon atom 8-40, styryl, vinyl phenanthryl are given, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propyl phenyl, carbinyl naphthyl, carbinyl phenanthryl, ethyl phenanthryl, propyl phenanthryl are given for 7-40 alkyl aryl number of carbon atom, vinyl, propenyl, cyclohexenyl are given for 2-10 alkenyl group number of carbon atom, for silicon component radical, radical same as the above is given, for oxygen component radical, aryl alkoxy group such as hydroxy radical, methoxy, ethoxy, propoxy, alkoxy group such as butoxy, phenoxy, methylphenoxy, dimethylphenoxy, ant Loki ti radical such as naphthoxy, phenylmethoxy, phenyl ethoxy gives られ.

For the sulfur component basis, スルフィネート radical such as substituent which oxygen of the oxygen component basis substituted sulfur for and carbinyl sulfonate, トリフルオロメタンスルフォネート, フェニルスルフォネート, ベンジルスルフォネート, p- トルエンスルフォネート, トリメチルベンゼンスルフォネート, トリイソブチルベンゼンスルフォネート, p- クロルベンゼンスルフォネート, スルフォネート radical such as ペンタフルオロベンゼンスルフォネート, メチルスルフィネート, フェニルスルフィネート, ベンゼンスルフィネート, p- トルエンスルフィネート, トリメチルベンゼンスルフィネート, ペンタフルオロベンゼンスルフィネート is given, for nitrogen component radical, amino group, methylamino, dimethylamino, diethylamino, dipropylamino, dibutylamino, alkylamino groups such as dicyclohexyl amino, phenylamino, diphenylamino, ditolylamino, dinaphthyl amino, arylamino radical such as methylphenyl amino or alkyl arylamino radical is given, for phosphorus component radical, dimethyl Foss fino, diphenyl Foss fino are given.

[0075]

Of these, it is preferable for R2 to be hydrogen atom or an alkyl group, and it is desirable that hydrogen atom in particular or carbinyl, ethyl, number of carbon atom

of propyl are 1-3 hydrocarbon group.

[0076]

2,7- dialkyl - fluorenyl bases are nominated for a preferred example for the fluorenyl basis having R2 as such a substituent, for alkyl group of 2,7- dialkyl of this case, 1-5 alkyl group is given number of carbon atom.

[0077]

In addition, R2 is same as R1 each other and may be different.

R3 and R4 are same each other and may be different, and 7-40 arylalkyl group, aryl alkenyl group of number of carbon atom 8-40, number of carbon atom are 7-40 alkyl aryl, silicon component radical, oxygen component radical, sulfur component radical, nitrogen component radical or phosphorus component radical 2-10 alkenyl group, number of carbon atom 6-20 aryl, number of carbon atom 1-10 alkyl group, number of carbon atom hydrogen atom same as the above, halogen atom, number of carbon atom.

[0078]

Of these, preferred R3 and number of carbon atom being 1-3 alkyl group on the other hand even if there is little R4.

X1 and X2 are same each other, and it may be different, and 1-20 hydrocarbon group, number of carbon atom are conjugated diene residue formed by 1-20 halogenation, hydrocarbon group, oxygen component radical, sulfur component radical or nitrogen component radical or X1 and X2, and hydrogen atom, halogen atom, number of carbon atom can exemplify atom same as the above or radical for halogen atom, oxygen component radical, sulfur component radical and nitrogen component radical for concreteness.

[0079]

Number of carbon atom, for 1-20 hydrocarbon group, alkyl groups such as carbinyl, ethyl, propyl, butyl, hexyl, cyclohexyl, octyl, nonyl, dodecyl, an Aiko sill, norbornyl, adamantyl,

Alkenyl group such as vinyl, propenyl, cyclohexenyl,

Arylalkyl group such as benzil, phenylethyl, phenylpropyl,

Aryl such as phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propyl phenyl,  $\alpha$  - or  $\beta$  - naphthyl, carbinyl naphthyl, anthryl, phenanthryl, benzil phenyl, pyrenyl, Ase naphthyl, phenalenyl, アセアントリレニル, a tetrahydronaphthyl, indanyl, biphenyl is given, the radical which halogen substituted 1-20 hydrocarbon group for the number of carbon atom for 1-20 halogenated hydrocarbon radical number of carbon atom is given.

[0080]

For conjugated diene residue formed from X1 and X2, four 1,4- 1,3-  $\eta$  - diphenyl

- butadiene, four 1,3-  $\eta$  - butadiene, four 1,4- 1,3-  $\eta$  - dibenzyl - butadiene, 4-1 1,3-  $\eta$  - phenyl - pentadiene, 4-3 1,3-  $\eta$  - carbonyl - pentadiene, four 1,4- 1,3-  $\eta$  - bis (trimethylsilyl) - butadiene, 2,3- dimethylbutadiene, four 2,4-  $\eta$  - hexadiene, isoprene are given.

[0081]

1,3- butadiene, 2,4- hexadiene, one 1,3- - phenyl - pentadiene, residue of 1,4- diphenyl butadiene are desirable, and, even more particularly, for conjugated diene residue formed from X1 and X2, number of carbon atom may be substituted these residue for in 1-10 hydrocarbon group.

[0082]

Of these, it is preferable for halogen atom, number of carbon atom to be 1-20 hydrocarbon group or the sulfur component bases.

As for Y, halogenation hydrocarbon group of 1-20 2 values, silicon component radical of 2 values, germanium component radical of 2 values, tin component radical of 2 values, -O-, -CO-, -S-, -SO-, -SO<sub>2</sub>-, -NR<sub>5</sub>-, -P(R<sub>5</sub>)-, -P(O) correct -, -BR<sub>5</sub>- or -AlR<sub>5</sub>- [hydrocarbon group of 1-20 2 values, number of carbon atom number of carbon atom (R<sub>5</sub>), 1-20 hydrocarbon group, number of carbon atom show 1-20 halogenated hydrocarbon radical] to R<sub>5</sub> hydrogen atom, halogen atom, number of carbon atom, for concreteness, number of carbon atom such as aryl alkylene group such as methylene, dimethyl methylene, 1,2- ethylene, 1,2- dimethyl - ethylene, 1,3- trimethylene, 1,4- tetramethylene, 1,2- cyclohexylene, alkylene group such as 1,4- cyclohexylene, diphenylmethylene, 1,2- diphenyl - ethylene, hydrocarbon group of 1-20 2 values,

The halogenation hydrocarbon group that the number of carbon atom halogenated hydrocarbon group of 1-20 2 values such as chloromethylene,

Silicon component radical of 2 values such as methylsilylene, dimethylsilylene, diethyl buttocks Ren, di(n- propyl) buttocks Ren, di(i- propyl) buttocks Ren, di(cyclohexyl) buttocks Ren, methylphenyl buttocks Ren, diphenyl buttocks Ren, di(p- tolyl) buttocks Ren, alkyl buttocks Ren of di(p- chlorophenyl) buttocks Ren, alkyl aryl buttocks Ren, aryl buttocks Ren radical, tetramethyl - 1,2- dibuttocks Ren, alkyl dibuttocks Ren of tetraphenyl - 1,2- dibuttocks Ren, alkyl aryl dibuttocks Ren, aryl dibuttocks Ren radical,

The germanium component basis of 2 values that substituted germanium for silicon of the silicon component basis of 2 values,

The tin component bases of 2 values that substituted tin for silicon of the silicon component basis of 2 values are given.

[0083]

Among the bases of these 2 values, the thing which the shortest joint of -Y- presented by regular expression (I) is atom of 1 or 2, and is constructed as is desirable.

In addition, as for R5, 1-20 hydrocarbon group, number of carbon atom are 1-20 halogenated hydrocarbon bases halogen atom same as the above, number of carbon atom.

[0084]

Of these, it is particularly desirable it depends on Y that preferred, it is silicon component radical of 2 values that number of carbon atom is hydrocarbon group of 1-5 2 values, the silicon component basis of 2 values or germanium component radical of 2 values, and preferred, to be alkyl buttocks Ren, alkyl aryl buttocks Ren or aryl buttocks Ren.

[0085]

In addition, the compound which replaced Zr with titanium or hafnium can be used in zirconium compound mentioned above.

In addition, for example, among the described above zirconium compound, the structure expression of Zr dichloride showed below dimethylsilylene (2, 7- 4, 5- two dimethyl - (- carbiny - benz) -1 - indenyl) (2, 7- di-t- butyl -9 - fluorenyl).

[0086]

[CHEMICAL FORMULA8]

[0087]

In addition, the structure expression of Zr dichloride showed below dimethylsilylene (2, 6- 4, 5- one dimethyl - (- carbiny - benz) -1 - indenyl) (2, 7- di-t- butyl -9 - fluorenyl).

[0088]

[CHEMICAL FORMULA9]

[0089]

These catalytic substances can be synthesized by the Japanese Patent Application No. 8-187563 bulletin that is an application concerning a this application person.

In addition, with the present invention, a compound expressed as metallocene compound (a) by the following regular expression (10) can be used.

[0090]

LaMX<sub>2</sub> ... (10)

In [regular expression (10), M is 周期率表第 IV group or metal of lanthanide series.

It is a derivative of the delocalization  $\pi$  association basis, and La is the radical which applies restraint geometric shape to metal M active site.

.] which is hydrocarbon group, silyl group or the germyl radical which X is independent respectively, and contain hydrogen, Halogen or carbon of less than or



equal to 20, silicon or germanium

In a compound presented by regular expression (10), chemical agent presented by the following regular expression (11) is desirable.

[0091]

[CHEMICAL FORMULA10]

[0092]

In regular expression (11), as for M, titanium, Zr or hafnium, X are similar to regular expression (10).

Cp couples  $\pi$  in M and it is permutation cyclopentadienyl group having substituent Z.

Element (for example, silicon, germanium or tin) of oxygen, sulfur, boron or 周期率表第 IVA group, Y are nitrogen, Lin, oxygen or ligand including sulfur, and Z may form condensed ring in Z and Y.

[0093]

Titanium dichloride is nominated for a compound presented by such a regular expression (11) silane) titanium dichloride (five 1,2- (t- butylamide) (tetramethyl -  $\eta$  - cyclopentadienyl) - ethanediyl) (dimethyl (t- butylamide) (five tetramethyl -  $\eta$  - cyclopentadienyl)).

[0094]

In addition, in the metallocene compound, the compound which substituted Zr or hafnium for titanium can be given.

A central metal atom is Zr, and, at a minimum, preferred, for metallocene compound (a) presented in regular expression (10) or (11), zirconocene chemical agent having ligand including two cyclopentadienyl skeletons is used.

In addition, it is desirable that a metal atom-centered in metallocene compound (a) presented in the regular expression (4) or (5) is titanium.

[0095]

According to the present invention, or metallocene compound (a) is put together more than two kinds alone, and it is used.

In addition, metallocene compound (a) dilutes in carbon hydride or halogenated hydrocarbon, and it may be used.

Even more particularly, metallocene compound (a) makes come in contact with carrier, and it can be used.

[0096]

Used carrier is an inorganic or organic compound, and preferably solid of form of granular of 20-200  $\mu\text{m}$  - corpuscle is used 10-300  $\mu\text{m}$  particle size.

Of these, a porous oxide is preferable, and, for example, as for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{ZnO}$ ,  $\text{BaO}$ ,  $\text{ThO}_2$  or these mixtures can exemplify  $\text{SiO}_2 - \text{MgO}$ ,  $\text{SiO}_2 - \text{Al}_2\text{O}_3$ ,  $\text{SiO}_2 - \text{TiO}_2$ ,  $\text{SiO}_2 - \text{V}_2\text{O}_5$ ,  $\text{SiO}_2 - \text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2 - \text{TiO}_2 - \text{MgO}$  for inorganic support concretely.

$\text{SiO}_2$  and the thing which, at a minimum, is based on one kind of constituent chosen among a group of  $\text{Al}_2\text{O}_3$  are desirable in these.

[0097]

In addition, even if a little  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{BaSO}_4$ ,  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , carbonate such as  $\text{Li}_2\text{O}$ , sulfate, nitrate, oxide constituent are contained in the inorganic oxide, it is put, and it cannot be used.

[0098]

As for such carrier, properties are different by the kind and formula, but 50-1000 $\text{m}^2/\text{g}$  are desirable, and specific surface is 100-700 $\text{m}^2/\text{g}$ , and, as for the carrier which it is preferable, and is used as the present invention, it is desirable that pore volume is 0.3-2.5 $\text{cm}^3/\text{g}$ .

100-1000 degrees Celsius are as necessary preferable, and the carrier burns at 150-700 degrees Celsius, and it is used.

[0099]

Even more particularly, for the carrier which can be applied to the present invention, form of granular of the organic chemistry that particle size is 10-300 $\mu\text{m}$  - corpuscle solid can be given.

These can exemplify ethylene, propylene, one-butene, the polymer which it is based on  $\alpha$ -olefin of carbon number 2-14 such as four-carbonyl-1-pentene, and is produced () or vinylcyclohexane, the polymer which it is based on styrene, and is produced or copolymer for an organic compound.

[0100]

Organoaluminum hydroxy-compound (b) used for the case when organoaluminum hydroxy-compound (b) forms a metallocene system catalytic substance next is explained.

[0101]

It may be well-known alumino oxane, and organoaluminum hydroxy-compound (b) used with the present invention may be organoaluminum hydroxy-compound (b) of benzene insolubility again.

[0102]

Alumino oxane of such public intellect is presented in the following regular expression (12) or (13) concretely.

[0103]

## [CHEMICAL FORMULA11]

[0104]

In [regular expression (12) and (13), R is hydrocarbon group such as methyl group, ethyl group, propyl group, butyl group, and preferably particularly preferably methyl group, ethyl group are methyl group, and m is .] which preferably is 5-40 integer numbers more than 2

In regular expression (12) or (13), alumino oxane may be formed by blending alkyloxy aluminium unit comprising alkyloxy aluminium unit [ here, R1 and R2 can exemplify hydrocarbon group same as R, R1 and R2 present the basis named difference] presented in alkyloxy aluminium unit presented in regular expression (OAl ( R1)) and general formula (OAl ( R2)).

[0105]

In addition, organoaluminum hydroxy- compound (b) used with the present invention may contain metal organic compound constituent except a little aluminium.

For example, alumino oxane such as the above can be prepared by means of a method such as follows.

[0106]

(1) A compound containing adsorption water or saline containing crystal water, a method, for example, organoaluminum compound such as trialkylaluminium is added in hydrocarbon medium suspension such as magnesium chloride hydrate, copper sulfate hydrate, aluminium sulfate hydrate, nickel sulfate hydrate, the first chloride cerium hydrate, and it is reacted, and to collect as solution of hydrocarbon.

[0107]

(2) A method direct water and ice and steam are triggered in organoaluminum compound such as trialkylaluminium in atmosphere such as benzene, toluene, ethyl ether, tetrahydrofuran, and to collect as solution of hydrocarbon.

[0108]

(3) A method to react organotin oxides such as dimethyl tin oxide, dibutyl tin oxide in organoaluminum compound such as trialkylaluminium in atmosphere such as decane, benzene, toluene.

[0109]

In addition, this alumino oxane may contain a little organic metal ingredient.

In addition, after solvent or unreacting organoaluminum compound was distilled from solution of the collected alumino oxane, and having removed, it may be dissolved in solvent again.

[0110]

It is concrete as organoaluminum compound used for case to prepare alumino oxane, trialkylaluminium such as trimethylaluminum, triethylaluminium, tripropyl aluminium, triisopropyl aluminium, trin- butyl aluminium, triisobutylaluminium, trisec- butyl aluminium, tritert- butyl aluminium, tripentyl aluminium, trihexyl aluminium, trioctyl aluminium, tridecyl aluminium,

Tricyclo alkylaluminum such as tricyclo hexyl aluminium, tricyclo octyl aluminium, Dialkyl aluminium halide such as dimethylaluminum chloride, diethylaluminium chloride, diethylaluminum bromide, a di-isobutyl aluminum chloride,

Dialkyl aluminium hydride such as diethylaluminum hydride, diisobutylaluminum hydride,

Dialkyl aluminium alkoxide such as dimethylaluminum methoxide, diethylaluminum ethoxide,

Dialkyl aluminium aryloxy dohs such as diethylaluminum phenoxide are given.

[0111]

Of these, trialkylaluminium and trialkyl aluminum are particularly preferable.

In addition, as this organoaluminum compound, regular expression (14)

(i- C<sub>4</sub>H<sub>9</sub>), xAl<sub>y</sub> (C<sub>5</sub>H<sub>10</sub>) z ... (14)

(it is a positive number, and x, y, z is  $z \geq 2x$ )

The isoprenyl aluminium which it attends, and is expressed can be used.

[0112]

Or organoaluminum compound such as the above is put together alone, and it is used.

For solvent used in the case of a preparation of alumino oxane, hydrocarbon solvent such as chlorinated matter, bromide is given benzene, toluene, xylene, cumene, aromatic hydrocarbon such as cymene, pentane, hexane, heptane, octane, decane, dodecane, hexadecane, aliphatic hydrocarbon such as octadecane, cyclopentane, cyclohexane, cyclooctane, alicycle family hydrocarbon such as methyl cyclopentane, gasoline, kerosine, petroleum fraction such as gas oil or the aromatic hydrocarbon, aliphatic hydrocarbon, halide of alicycle family hydrocarbon especially.

In addition, ether such as ethyl ether, tetrahydrofuran can be used.

Aromatic hydrocarbon in particular is preferable among these solvent.

[0113]

In addition, the Al ingredient that organoaluminum hydroxy- compound of the benzene insolubility dissolves in benzene of 60 degrees Celsius is Al atom conversion, and preferably particularly preferably lower than 5% are lower than 2%, and lower than 10% are insolubility or poor solubility for benzene.

[0114]

After suspension did the organoaluminum hydroxy- compound that solubility as opposed to benzene of such an organoaluminum hydroxy- compound was equivalent to Al of 100mg atom in benzene of 100ml, after having been mixed at agitation bottom 60 degrees Celsius for six hours, product made in jacket G-5 glass filter belonging to is used, it is filtered at 60 degrees Celsius at heat time, is demanded by measuring abundance (x millimole) of the Al atom which there is by the end of all filtrate after benzene 50ml of 60 degrees Celsius are used, and having washed solid part separated on filter four times (x %).

[0115]

For ionization ionic compound (c) ionization ionic compound (when it is called ionicity ionizing compounds, ionic compound, there is) (c), Lewis acid, ionic compound, a borane compound and a carborane compound can be exemplified.

[0116]

Mg component Lewis acid, Al component Lewis acid, B component Lewis acid are nominated for Lewis acid, of these, B component Lewis acid is preferable.

For B component Lewis acid, BR<sub>3</sub> (R shows phenyl group or the fluorine atom which may have substituent such as fluorine atom, methyl group, trifluoromethyl group.)

It is the compound which it appears, and is presented, and trifluoro boron, triphenyl boron, tris (four-fluorophenyl) boron, tris (3,5-difluorophenyl) boron, tris (four-fluoromethyl phenyl) boron, tris (pentafluorophenyl) boron, tris (p-tolyl) boron, tris (o-tolyl) boron, tris (3,5-dimethyl phenyl) boron are given to be concrete.

[0117]

Ionic compound is salt becoming a cationic compound from an anionic compound, and anion makes metallocene chemical agent (a) cation by what is responded with metallocene chemical agent (a), there is function making stabilize transition metal cation seed by forming ion pair.

For such an anion, there are organoboron compound anion, organoarsenical anion, organoaluminum anion, a thing making it is comparatively bulky, and stabilize transition metal cation seed is desirable.

Metal cation, organic metal cation, carbonium cation, トリピウムカチオン, oxonium cation, sulfonium cation, phosphonium cation, ammonium cation are nominated for cation.

More particularly, it is triphenyl carbenium cation, tributyl ammonium cation, N, N-dimethyl ammonium cation, フェロセニウムカチオン.

[0118]

Dialkyl ammonium salt such as N, N-dialkyl anilinium salt, dialkylammonium salt,

travelling substituted ammonium salts such as トリアリールホスフォニウム salt, triethylammonium tetra (phenyl) boron, tripropylammonium tetra (phenyl) boron, travelling substituted ammonium salts such as tri (n- butyl) ammonium tetra (phenyl) boron, di (one - propyl) ammonium tetra (pentafluorophenyl) boron, dicyclohexyl ammonium tetra (phenyl) boron is given as such an ionic compound to be concrete.

[0119]

In addition, triphenyl carbenium tetrakis (pentafluorophenyl) borate, N, N- dimethyl anilinium tetrakis (pentafluorophenyl) borate, フェロセニウムテトラ (pentafluorophenyl) borate can be nominated for ionic compound containing boron atom.

[0120]

For the borane compound, decaborane (14),

Screw [bird (n- butyl) ammonium] Nona borate, screw [bird (n- butyl) ammonium] deca borate, screw [bird (n- butyl) ammonium] screw (dodeca hydride dodeca borate) nickelic acid salt (salt of metal borane anion such as III) is given.)

[0121]

For the carborane compound, salt of metallacarborane anion such as four - carba nonaborane (14), 1, 3- dicarba nonaborane (13), screw [bird (n- butyl) ammonium] screw (undeca hydride -7 - carba undeca borate) nickelic acid salt (IV) is given.

[0122]

Or ionization ionic compound (c) such as the above is put together more than two kinds alone, and it is used.

In addition, it makes the carrier compound carry organoaluminum hydroxy- compound (b) and ionization ionic compound (c), and it can be used.

[0123]

In addition, if a metallocene system catalytic substance is prepared, when it is done in case, with organoaluminum hydroxy- compound (b) or ionization ionic compound (c), organoaluminum compound (d) may be used if necessary.

[0124]

For organoaluminum compound (d) used depending on organoaluminum compound (d) requirement, the organoaluminum compound which, for example, is presented in follows general formula (15) can be exemplified.

[0125]

$R_1nAlX_{3-n} \dots$  (15)

(among expression (15),  $R_1$  is hydrocarbon group of carbon number 1-12, and  $X$  is halogen atom or hydrogen atom, and  $n$  is 1-3.)

For example, in the regular expression (15), as for  $R_1$ , hydrocarbon group of carbon

number 1-12 is an alkyl group, cycloalkyl groups or the ant - rous basis, but it is methyl group, ethyl group, n- propyl group, isopropyl group, isobutyl group, pentyl group, a hexyl group, octyl radical, cyclo pentyl group, cyclohexyl group, phenyl group, tolyl group to be concrete.

[0126]

The following compounds are used as such organoaluminum compound (d) to be concrete.

Trialkylaluminium such as trimethylaluminum, triethylaluminium, triisopropyl aluminium, triisobutylaluminium, trioctyl aluminium, two tri- ethylhexyl aluminium,

Alkenyl aluminium such as isoprenyl aluminium,

Dialkyl aluminium halide such as dimethylaluminum chloride, diethylaluminium chloride, diisopropyl aluminium chloride, a di-isobutyl aluminum chloride, dimethylaluminum bromide,

Alkylaluminum sesqui halide such as carbanyl aluminium sesqui chloride, ethylaluminium sesquichloride, isopropyl aluminium sesqui chloride, butyl aluminium sesqui chloride, ethyl aluminium sesqui bromide,

Alkylaluminum dihalide such as carbanyl aluminium dichloride, ethylaluminum dichloride, isopropyl aluminium dichloride, ethyl aluminium dibromide,

Alkylaluminum hydride such as diethylaluminum hydride, diisobutylaluminum hydride.

[0127]

In addition, a compound expressed as organoaluminum compound (d) by the following regular expression (16) can be used.

$R_1nAlY_{3-n} \dots$  (16)

(among expression (16),  $R_1$  is similar to the above, and  $Y$  is the -  $OR_2$  basis, the -  $OSiR_3$  basis, the -  $OAlR_4$  basis, -  $NR_5$  radical, -  $SiR_6$  radical or -  $N$  ( $R_7$ )  $AlR_8$  radical, and  $n$  is one or two, and  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_8$  are methyl group, ethyl group, isopropyl group, isobutyl group, cyclohexyl group, phenyl group, and  $R_5$  is hydrogen atom, methyl group, ethyl group, isopropyl group, phenyl group, trimethylsilyl group, and  $R_6$  and  $R_7$  are methyl group, ethyl group.)

The following compounds are used as such an organoaluminum compound to be concrete.

(1) A compound presented in  $R_1nAl(OR_2)_{3-n}$ , for example, as for the dimethylaluminum methoxide, the diethylaluminum ethoxide, the diisobutylaluminum methoxide,

(2) A compound presented in  $R_1nAl(OSiR_3)_{3-n}$ , for example, as for  $Et_2Al(OSiMe_3)$ , the (iso-Bu) $_2Al(OSiMe_3)$ , the (iso-Bu) $_2Al(OSiEt_3)$ ,

(3) A compound presented in  $R_1nAl(OAlR_4)_{3-n}$ , for example,  $Et_2AlOAlEt_2$ , (iso-Bu) $_2AlOAl(iso-Bu)$ , as for 2,

(4) A compound presented in  $R_1nAl(NR_5)_{3-n}$ , for example,  $Me_2AlNEt_2$ ,  $Et_2AlNHMe$ ,

Me<sub>2</sub>AlNH<sub>2</sub>Et, Et<sub>2</sub>AlN(SiMe<sub>3</sub>)<sub>2</sub>, (iso-Bu)<sub>2</sub>AlN(SiMe<sub>3</sub>), as for 2,

(5) A compound presented in R<sub>n</sub>Al(SiR<sub>63</sub>)<sub>3-n</sub>, for example, (as for iso-Bu)<sub>2</sub>AlSiMe<sub>3</sub>

(6) R<sub>n</sub>Al (compound presented in N(R<sub>7</sub>)AlR<sub>82</sub>)<sub>3-n</sub>, for example, Et<sub>2</sub>AlN(Me)AlEt<sub>2</sub>, (iso-Bu)<sub>2</sub>AlN(Et)Al(iso-Bu)<sub>2</sub>.

[0128]

The regular expression (15) and chemical agent expressed in general formula R<sub>13</sub>Al, R<sub>n</sub>Al(OR<sub>2</sub>)<sub>3-n</sub>, R<sub>n</sub>Al(OAlR<sub>42</sub>)<sub>3-n</sub> in things of organoaluminum compound presented in (16) are desirable, and R is isoalkyl group particularly, and the chemical agent which is n = 2 is desirable.

[0129]

With the inter-polymerization present invention of ethylene /  $\alpha$  - olefin copolymer [A], copolymerization can usually put  $\alpha$  - olefin of ethylene and carbon number 4-20 in an existence bottom of metallocene chemical agent (a) such as the above and organoaluminum hydroxy- compound (b) and ionization ionic compound (c) and catalyst formed as necessary by organoaluminum compound (d) in liquid phase.

In doing so, hydrocarbon solvent is used to the public, but  $\alpha$  - olefin may be used as solvent.

[0130]

This inter-polymerization can be done in batch type, half continuous system, both methods of continuous system.

If inter-polymerization is performed in batch method, when it is done in case, the catalyst component is used in the following density.

[0131]

When metallocene system catalyst to become is used by metallocene compound (a) and organoaluminum hydroxy- compound (b) or ionization ionic compound (c), 0.00005-0.1 millimeters mol / liter (a polymerization capacity) is usually desirable for density of metallocene chemical agent (a) in polymerization system, and it is 0.0001-0.05 millimeters mol / liter.

In addition, preferably, as for organoaluminum hydroxy- compound (b), it is supplied 1-10000 in 10-5000 quantity in mole ratio (Al/ transition metal) of aluminium atom as opposed to transition metal in a metallocene compound in polymerization system.

[0132]

0.5-20 are preferable, and, in that case of ionization ionic compound (c), it is supplied in 1-10 quantity in mole ratio (ionization ionic compound (c) / metallocene compound (a)) of ionization ionic compound (c) as opposed to metallocene compound (a) in polymerization system.



[0133]

In addition, about 0-5 millimeters mol / liters (a polymerization capacity) are usually preferable, and it is used as about 0-2 millimeters mol / liters in the quantity that it is when organoaluminum compound is used.

[0134]

It is preferable to +150 degrees Celsius reaction temperature -20, and preferably, 0-120 degrees Celsius, pressure exceeds zero at 0-100 degrees Celsius, and preferably the 8MPa (80kgf/cm<sup>2</sup>, hydraulic line pressure) following exceeds zero 7, and, as for the copolymerization reaction, it is usually performed 4 in a condition bottom of less than or equal to 9MPa (50kgf/cm<sup>2</sup>, hydraulic line pressure)..

[0135]

Ethylene and  $\alpha$  - olefine are supplied in polymerization system in the quantity that ethylene /  $\alpha$  - olefin copolymer [A] of the particular composition is provided.

On the occasion of inter-polymerization, molecular weight modifier such as hydrogen can be used.

[0136]

It is usually provided as polymerization fluid including ethylene /  $\alpha$  - olefin copolymer [A] when it makes it is done as above, and do copolymerization in ethylene and  $\alpha$  - olefin.

This polymerization liquid is processed by conventional method, ethylene /  $\alpha$  - olefin copolymer [A] is provided.

[0137]

Ethylene system copolymer [B] used with the ethylene system copolymer [B] present invention is copolymer with at least none of chemical agent chosen by group comprising  $\alpha$  - olefin of ethylene and carbon number 3-20, cyclic olefin system chemical agent or aromatic vinyl compound.

[0138]

For  $\alpha$  - olefin, propene, one - butene, one - pentene, one - hexene, three - carbiny 1 - butene, three - carbiny 1 - pentene, three - ethyl 1 - pentene, four - carbiny 1 - pentene, four - carbiny 1 - hexene, 4,4- dimethyl 1 - pentene, four one - ethyl 1 - hexene - octene, three - ethyl 1 - hexene, one - octene, one - decene, one - dodecen, one - tetradecene, one - hexadecene, one - octadecene, one - eicosen are given to be concrete.

Of these, it is preferable, and propene, one - butene, one - hexene, four - carbiny 1 - pentene, one - octene are used.

[0139]

Cyclic olefin presented in the following regular expression (17) or (18) is nominated for cyclic olefin.

[0140]

[CHEMICAL FORMULA12]

[0141]

In the expression, n is zero or 1, and m is zero or a positive integer, and k is zero or 1.

In addition, as for ring 6 which k uses k in the event of 1, and is presented, it is with membered-ring, as for this ring, it is in five-member in the event of zero k.

[0142]

R1 - R18 and Ra and Rb are independent respectively, and it is hydrogen atom, halogen atom or hydrocarbon group.

Here, halogen atom is fluorine atom, chlorine atom, bromine atom or iodine atom.

[0143]

Even more particularly, R15 and R18 or R16 and R17 couple respectively (and it is shared each other), and, in the regular expression (18), R16 and R18 may form radical of monocycle or polycyclic R15 and R17 R17 and R18 R15 and R16, monocycle or the polycyclic which, besides, is formed in this way may have double bond.

[0144]

[CHEMICAL FORMULA13]

[0145]

In the expression, p and q are independent respectively, and it is zero or an equilateral integer number, and stand-alone respectively, r and s are zero, 1 or 2.

In addition, R21 - R39 is independent respectively, and it is hydrogen atom, halogen atom, hydrocarbon group or alkoxy group.

[0146]

Halogen atom is the same as the halogen atom of the general formulae (17) here.

In addition, an alkyl group of number of carbon atom 1-20, cycloalkyl groups of number of carbon atom 3-15 or aromatic hydrocarbon radical is usually nominated for hydrocarbon group.

For an alkyl group of number of carbon atom 1-20, methyl group, ethyl group, propyl group, isopropyl group, amyl group, a hexyl group, octyl radical, decyl, dodecyl group and octadecyl group are given to be concrete.

An alkyl group may be substituted these for in halogen atom.

[0147]

Cyclohexyl group is nominated for cycloalkyl groups, aryl, aralkyl group are nominated for aromatic hydrocarbon radical, phenyl group, tolyl group, naphthyl group, benzyl group, phenylethyl radical are given to be concrete.

[0148]

Methoxy group, ethoxy group, a propoxy group are nominated for alkoxy group.

Or, with the carbon atom which carbon atom or R31 which carbon atom and R33 which R29 and R30 couple here couple couples, alkylene group of number of carbon atom 1-3 is gone through directly, and it may be coupled.

In other words when two carbon atom goes through alkylene group, and it is coupled, R29 and R33 or R30 and R31 share each other, and either alkylene group in a thing of methylene group (-CH<sub>2</sub>-), ethylene group (-CH<sub>2</sub>CH<sub>2</sub>-) or propylene group (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-) is formed.

[0149]

Even more particularly, it is coupled to R35 and R32 or R35 and R39 each other, and, at the time of  $r = s = 0$ , aromatic ring of monocycle or polycyclic may be formed.

For cyclic olefin presented in regular expression (17) such as the above or (18), bicyclo -2 - heptenes (a bicyclo hept -2 - エン derivative), tricyclo -3 - decenes, tricyclo -3 - undecene derivative, tetracyclo -3 - doh decenes, pentacyclo -4 - pentadecene derivative, pentacyclo pentadecadiene derivative, pentacyclo -3 - pentadecene derivative, pentacyclo -3 - hexadecene derivative, pentacyclo -4 - hexadecene derivative, ヘキサシクロ -4 - hepta decenes, heptacyclo -5 - eicosen derivative, heptacyclo -4 - eicosen derivative, heptacyclo -5 - strange eicosen derivative, オクタシクロ -5 - ドコセン derivative, Nona cyclo -5 - pen octopus sen derivative, Nona cyclo -6 - ヘキサコセン derivative, cyclopentadiene - acenaphthylene appendage, 1,4- methano -1,4,4a,9a- tetrahydro fluorenes, 1,4- methano -1,4,4a,5,10,10a- hexahydro anthracenes are given concretely.

[0150]

For aromatic vinyl compound, styrene,

o- methylstyrene, o- methylstyrene, m- methylstyrene, p- methylstyrene, o, p- dimethylstyrene, o- ethyl styrene, m- ethyl styrene, things such as p- ethyl styrene or poly alkyl styrene,

Functional group component styrene derivatives such as methoxystyrene, ethoxy styrene, vinyl benzoic acid, vinyl methyl benzoate, vinylbenzyl acetate, hydroxystyrene, o- chlorostyrene, p- chlorostyrene, divinylbenzene,

Three - phenyl propylene, four - phenyl butene,  $\alpha$  - methylstyrene are given.

Or these aromatic vinyl compound puts one kind together more than two kinds alone.

and it can be used.

(i) Content of a constitutional unit guided by ethylene is 99-90 mol %, and it is desirable for ethylene system copolymer [B] used with the content present invention of each constitutional unit in ethylene system copolymer [B] that content of the constitutional unit which, at a minimum, is guided by chemical agent of one chosen by  $\alpha$  - olefin of carbon number 3-20, cyclic olefin and aromatic vinyl compound is 1-10 mol %.

(ii) 0.890-0.940g/cm<sup>3</sup> are desirable, and there is apparent density of board of ethylene system copolymer [B] used with the apparent density of board present invention in field of 0.895-0.940g/cm<sup>3</sup>.

(iii) Preferably there are 190 degrees Celsius of ethylene system copolymer [B] used with the melt flow rate (MFR) present invention, melt flow rate in 2.16kg load for 0.3-50g /10 in a range for 0.5-20g /10.

(iv)  $<400^{\circ}\text{Tm d-250}$  is desirable, and preferably than  $<450^{\circ}\text{Tm d-297}$  temperature (Tm) and density (d) of maximum peak location in endotherm curve measured in maximum peak location temperature and apparent density of board differential scanning type calorimeter (DSC) satisfy the relationship that particularly preferred, is shown  $<500^{\circ}\text{Tm d-344}$  to in  $<550^{\circ}\text{Tm d-391}$ .

[0151]

In addition, it is desirable that melt flow rate (MFR) measured in melt tension (MT) in room temperature and 190 degrees Celsius, 2.16kg load as well as (i) - (iv) satisfies the relationship that is  $2.2^{\circ}\text{MT} \leq \text{MFR}$  sets to love .84s as for ethylene /  $\alpha$  - olefin copolymer [B] used with the present invention.

[0152]

Even more particularly, ethylene /  $\alpha$  - olefin copolymer [B] which is used with the present invention, n-decane soluble constituent quantity fraction (W (% by weight)) in room temperature and density,

(a) At the time of for  $\text{MFR} \leq 10\text{g} / 10$ , it is  $<80^{\circ}\text{W exp}(-100(d-0.88)) + 0.1\text{s}$   
Preferably it is  $<60^{\circ}\text{W exp}(-100(d-0.88)) + 0.1\text{s}$

More preferably, a relationship shown to is filled with  $<40^{\circ}\text{W exp}(-100(d-0.88)) + 0.1\text{s}$ ,

(b) It depends to fill a relationship shown to with  $<80^{\circ}\text{(MFR-9) } 0.26^{\circ}\text{W exp}(-100(d-0.88)) + 0.1\text{s}$  and, at the time of for  $\text{MFR} > 10\text{g} / 10$ , is desirable.

[0153]

Production method such ethylene system copolymer [B] of ethylene system copolymer [B] can produce at least one chemical agent chosen as an existence bottom of

above-mentioned metallocene system catalyst by  $\alpha$  - olefin of ethylene and carbon number 3-20, cyclic olefin or aromatic vinyl compound by making do copolymerization.

For example, the following compounds are nominated for a metallocene system catalytic substance.

[0154]

Screw (cyclopentadienyl) Zr dichloride, screw (methylcyclopentadienyl) Zr dichloride, screw (ethyl cyclopentadienyl) Zr dichloride, screw (n- propyl cyclopentadienyl) Zr dichloride, screw (n- butylcyclopentadienyl) Zr dichloride, bis (n- hexyl cyclopentadienyl) Zr dichloride, bis (carbanyl -n- propyl cyclopentadienyl) Zr dichloride, bis (carbanyl -n- butylcyclopentadienyl) Zr dichloride, bis (dimethyl -n- butylcyclopentadienyl) Zr dichloride, bis (n- butylcyclopentadienyl) Zr dibromide, bis (n- butylcyclopentadienyl) Zr methoxy chloride, bis (n- butylcyclopentadienyl) Zr ethoxy chloride,

Screw (n- butylcyclopentadienyl) Zr butoxy chloride, screw (n- butylcyclopentadienyl) Zr ethoxide, screw (n- butylcyclopentadienyl) Zr methyl chloride, screw (n- butylcyclopentadienyl) Zr dimethyl, bis (n- butylcyclopentadienyl) Zr benzyl chloride, bis (n- butylcyclopentadienyl) Zr dibenzyl, bis (n- butylcyclopentadienyl) Zr phenyl chloride, bis (n- butylcyclopentadienyl) Zr hydride chloride.

In addition, in the illustration, as for disubstituted body 1, 2- of cyclopentadienyl ring and 1, 3- substitution product are included.

In addition, with the present invention, the metallocene chemical agent which replaced Zr metal with titanium metal or hafnium metal can be used in zirconium compound such as the above.

[0155]

The second ethylene /  $\alpha$  - olefin copolymer composition explains the second ethylene /  $\alpha$  - olefin copolymer concerning the present invention next.

[0156]

Preferably preferably, as for the second ethylene /  $\alpha$  - olefin copolymer composition concerning the present invention, it is from 10-50 % by weight 1-70 % by weight 90-50 % by weight and high density polyethylene [C] 99-30 % by weight ethylene /  $\alpha$  - olefin copolymer [A].

[0157]

In addition, as for ethylene /  $\alpha$  - olefin copolymer [A], a thing same as the above is used.

High density polyethylene [C]

High density polyethylene [C] which is employed for the present invention,

(i)

0.945-0.970g/cm<sup>3</sup> are preferable, and there is apparent density of board in a range of 0.945-0.960g/cm<sup>3</sup>,

(ii) There are 190 degrees Celsius, melt flow rate (MFR) in 2.16kg load in 0.5-20 ranges for 0.3-50g/10.

[0158]

Such, high density polyethylene [C] can be got in well-known production method conventionally.

In other words high density polyethylene [C] can be produced by making or existence of a catalytic substance polymerizes ethylene alone below or do copolymerization with a little  $\alpha$  - olefin which seems to be lower than 1 mol %.

As the catalytic substance, it is concrete,

(1) A titanium system catalytic substance consisting of solid titanium catalyst component and organoaluminum compound,

(2) It is extended a vanadium system catalyzer to become by soluble vanadium compound and organoaluminum compound

(3) Metallocene system catalytic substances are given.

[0159]

A solid titanium catalyst component is prepared by titanium compound such as follows, magnesium compound and making electron donor come in contact.

A method to melt-knead ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B] or high density polyethylene [C] for methods for preparing of ethylene /  $\alpha$  - olefin copolymer composition concerning the preparation present invention of ethylene /  $\alpha$  - olefin copolymer composition, solution for a hermaphrodite are blended, and a method to remove solvent, one constituent are going to be molten condition, and methods to supply the other constituent with solid condition or molten condition are given.

[0160]

Ethylene /  $\alpha$  - olefin copolymer composition of the present invention which it is done as above, and is provided is useful as modifying agent of chip resistance of thermoplastic resin and rigidity.

For such a thermoplastic, polyolefin, polyamide, polyester, polystyrene, poly, polyvinyl alcohol can be exemplified.

In addition, grafting may denature ethylene /  $\alpha$  - olefin copolymer composition concerning the present invention by unsaturated carboxylic acid when property

modification assumes polar group component thermoplastic.

[0161]

From the ethylene /  $\alpha$  - olefin copolymer composition, pellet is molded by extrusion or injection molding so that ethylene /  $\alpha$  - olefin copolymer composition concerning the present invention is used, and property modification does resin such as polypropylene, it is melt blended ればよい in the resin that reforming is going to do this pellet.

[0162]

By such a resinous property modification method, it is desirable to use equipment it is kneaded continually, and to drain such as extruder.

As for kneading, more than a resinous melt point or the flexibility point which is going to be drained and a thing performed in less than 400 degrees Celsius are desirable.

[0163]

When ethylene /  $\alpha$  - olefin copolymer composition concerning such present invention is used as modifying agent, reforming can do chip resistance in cryogenic temperature and pulling elongation hardness particularly with having kept resinous rigidity such as polypropylene resin.

[0164]

The first propylene system polymer composition concerning the propylene system polymer composition present invention is propylene system polymer [D] and the composition that it is from ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B].

[0165]

Preferably 98-60 % by weight is 95-65 % by weight, and 2-40 % by weight is desirable for total) of content ([A] of ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B] and [B], and content of propylene system polymer [D] in the first such propylene system polymer composition is 5-35 % by weight.

[0166]

In addition, 99/1-30/70 are desirable for ratio ([A] / [B]) of content with ethylene /  $\alpha$  - olefin copolymer [A] and ethylene system copolymer [B] to be able to put by the end of the first propylene system polymer composition, and it is 90/10-50/50.

[0167]

The second propylene system polymer composition concerning the present invention is propylene system polymer [D] and the composition that it is from ethylene /  $\alpha$  - olefin copolymer [A] and high density polyethylene [C].

[0168]

Preferably 98-60 % by weight is 95-65 % by weight, and 2-40 % by weight is desirable for total) of content ([A] of ethylene /  $\alpha$  - olefin copolymer [A] and high density polyethylene [C] and [C], and content of propylene system polymer [D] in the second such propylene system polymer composition is 5-35 % by weight.

[0169]

In addition, 99/1-30/70 are desirable for ratio ([A] / [C]) with content and high density polyethylene [C] of ethylene /  $\alpha$  - olefin copolymer [A] to be able to put by the end of the second propylene system polymer composition, and it is 90/10-50/50.

[0170]

When such a propylene system polymer composition measured temperature dependency of degree of elasticity every 3 degrees Celsius, and it was plotted, it is desirable there is peak of an attenuation factor ( $\tan \delta$ ) due to glass transformation temperature of peak of an attenuation factor ( $\tan \delta$ ) due to glass transformation temperature of propylene system polymer [D] and ethylene /  $\alpha$  - olefin copolymer composition and that both peak separates.

In addition, when two peaks appear definitely, in other words the case that there is saddle between between the highest score of two peaks is judged to 'separate'.

Such an olefinic system resin composition is superior in chip resistance and balance with stiffness properties.

[0171]

In addition, preferably, more than 20, balance of rigidity and pulling elongation at breakage and cryogenic temperature impulsiveness be superior to a case with the use of 40-200 propylene system polymer, and, besides, MFR measured with 230 degrees Celsius, 2.16kg load as propylene system polymer [D] can get superior propylene system polymer composition in flowability.

[0172]

As for propylene system polymer [D] propylene system polymer [D], homopolymer of propylene or propylene and ethylene or number of carbon atom is copolymer with 4-20  $\alpha$  - olefin.

Ethylene, one - butene, one - pentene, four - carbonyl -1 - pentene, one - hexene, one - octene, one - decene, one - dodecane, one - tetradecene, one - hexadecene, one - octadecene, one - eicosane are given for 4-20  $\alpha$  - olefin number of carbon atom.

Or these one kind of  $\alpha$  - olefin is put together more than two kinds alone, and it can be used.

These  $\alpha$  - olefin may form propylene and random copolymer, in addition, block



copolymer may be formed.

According to the present invention, preferred crystallinity propylene ethylene random copolymer of 0.5-10 mol % crystallinity propylene ethylene block copolymer of 2-40 mol %, ethylene content propylene homopolymer, ethylene content.

[0173]

Preferably, even more particularly, preferably, in such propylene system polymer [D], as for the melt flow rate measured with 230 degrees Celsius, 2.16kg load, a thing in field for 20-200g/10 is desirable for 20-400g/10 more than normal 0.1g/10 minute.

According to the present invention, effect is big property modification in the propylene system polymer that MFR in particular is older than for 40g/10 when it is done.

[0174]

In addition, preferably, as for the apparent density of board of such propylene system polymer [D], 0.890-0.910g/cm<sup>3</sup>, the thing which it stops, and preferably there is in field of 0.895-0.910g/cm<sup>3</sup> are desirable normal 0.885-0.910g/cm<sup>3</sup>.

Even more particularly, 1.490-1.510 are usually preferable, and 1.495-1.510 get together, and preferably there is an index of refraction of such propylene system polymer [D] in 1.500-1.510 field.

[0175]

Propylene system polymer [D] having such a characteristic properties can be produced by various kinds of methods, but, for example, the catalyst that catalyst formed by high activity titanium catalyst formed by both constituent and electron donor or metallocene chemical agent and alumino xanthan gum or these catalyst was mixed is used as catalytic substance formed by a solid titanium catalyst component and organometallic compound catalyst component or these, and it can be produced.

In addition, different catalyst chosen every each stage by the catalyst is used, and it can be produced in multistage polymerization when propylene system polymer [D] is block copolymer.

[0176]

There is not limiting in particular, and a formula of an olefinic system resin composition concerning the preparation present invention of propylene system polymer composition can knead ethylene /  $\alpha$  - olefin copolymer [A], ethylene system copolymer [B] or high density polyethylene [C] and propylene system polymer [D] collectively, it can be produced by, in addition, kneading propylene system polymer [D] and the ethylene /  $\alpha$  - olefin copolymer composition of the first or the second by conventionally well-known methods such as alligation by internal mixer such as Vamba

Lee first detector, kneader, intermixture.

According to the present invention, the latter is preferable from a period of working properties.

[0177]

In addition, by a preparation of propylene system polymer composition concerning the present invention, styrene block copolymer may be put in the range that does not lose object of the invention.

Styrene and block copolymer of a conjugated diene compound are nominated for styrene block copolymer.

[0178]

For this styrene, styrene,  $\alpha$ -methylstyrene, p-methylstyrene, alkyl styrene of a p-t-butylstyrene window, p-methoxystyrene, vinyl naphthalene and these combination are given.

Of these, styrene is preferable.

[0179]

For a conjugated diene compound, butadiene, isoprene, piperylene, carbinyl pentadiene, phenylbutadiene, 3,4-1,3-dimethyl-hexadiene, 4,5-1,3-diethyl-octadiene and these combination are given.

Butadiene, isoprene are preferable in these.

[0180]

For such a styrene block copolymer, styrene butadiene block copolymer, styrene butadiene styrene bird block copolymer, styrene isoprene diblock copolymer, styrene isoprene styrene bird block copolymer, hydrogen additives of styrene butadiene diblock copolymer, hydrogen additives of styrene butadiene styrene triblock copolymer, hydrogen additives of styrene isoprene diblock copolymer, hydrogenation thing of styrene isoprene styrene triblock copolymer can be given to be concrete.

[0181]

According to the present invention, what weight ratio of a constitutional unit led by a constitutional unit and conjugated diene chemical agent derived from a styrene system compound uses 10/90-65/35, the styrene block copolymer which preferably is 20/80-50/50 as is desirable.

[0182]

In addition, molecular structure of this styrene block copolymer may be both such as linear, form of branching, radial or these configuration.

In addition, with the present invention, additive such as nucleating additive, oxidation inhibitor, hydrochloric acid absorbent, tenderizer, light stabilizer, UV

absorber, lubricant, age resistor, processing aid, heat stabilizer resistance, weathering agent, antistat, fire retardant, pigment, color, dispersing agent, copper inhibitor, neutralizer, blister agent, plasticizer, bubble inhibitor, crosslinking agent, current such as peroxide-related conditioner, Weld hardness conditioner, antifog additive can be blended in the field which does not lose object of the invention besides ethylene /  $\alpha$  - olefin copolymer composition and propylene system polymer [D].

In addition, well-known inorganic fillers such as purified talc, a fiber glass may be blended.

For this case, it is desirable for an inorganic filler as against 100 propylene polymer composition part by weight that it is blended 1-40 part by weight.

[0183]

Propylene system polymer composition concerning the present invention can be molded as various molded articles such as a film, sheet, pipe by forming processes such as extrusion, injection molding, inflation molding, a calendar plastic treatment.

A provided molded article is superior in distortion recovery properties.

[0184]

A resinous property modification method concerning the resinous property modification method present invention is characterized by resin and the melt blended which are going to do reforming doing は, pellet comprising the ethylene /  $\alpha$  - olefin copolymer composition of the first or the second.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since it consists of ethylene and a specific alpha olefin copolymer, and a specific specific ethylene system copolymer, when it is used as reforming material of thermoplastics, especially polypropylene, the 1st ethylene and alpha olefin copolymer constituent of this invention can raise the rigidity of resin, and the balance of \*\*\*\* fracture point elongation, and workability is still better [ a constituent ] in order that it may not cause blocking etc. in the case of reforming.

[0186] Since it consists of specific ethylene and alpha olefin copolymer, and specific high density polyethylene, when it is used as reforming material of thermoplastics, especially polypropylene, the 2nd ethylene and alpha olefin copolymer constituent of this invention can raise the rigidity of resin, and the balance of \*\*\*\* fracture point elongation, and workability is still better [ a constituent ] in order that it may not cause blocking etc. in the case of reforming.

[0187] Since the 1st propylene system polymer constituent of this invention contains the specific ethylene and alpha olefin copolymer, and the specific ethylene system copolymer, it is excellent in the rigidity of resin, and the balance of \*\*\*\* fracture point elongation. Moreover, since the 2nd propylene system polymer constituent of this invention contains specific ethylene and alpha olefin copolymer, and specific high density polyethylene, it is excellent in the rigidity of resin, and the balance of \*\*\*\* fracture point elongation.

[0188] By the reforming approach of the resin concerning this invention, since the above ethylene and alpha olefin copolymer constituents are used, on the occasion of reforming of thermoplastics, blocking etc. cannot take place easily and it excels in operability and the productivity of reforming thermoplastics.

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[Translation done.]

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EXAMPLE

[Example] Hereafter, although an example explains this invention, this invention is not limited to these examples at all.

[0190] In addition, the physical properties of each resinous principle are the following, and were made and evaluated.

1. After heat-treating physical-properties [consistency] 190 degree C of ethylene and an alpha olefin copolymer [A], and the strand after the MFR measurement in 2.16kg load for 1 hour and annealing them to a room temperature over 1 hour at 120 degrees C, it measured with the density gradient tube method.

[0191] The [alpha olefin content, T\*\*\*\*/T\*\*\*\*, and B value] 13 C-NMR spectrum determined.

[Limiting viscosity [eta]] It measured in 135 degrees C and a decalin.

[0192] It measured at 140 degrees C with the alt.dichlorobenzene solvent using [Mw/Mn] GPC (gel permeation chromatography).

[0193] [MFR10/MFR2] ASTM Based on D-1238, MFR10 in 10kg load in 190 degrees C and MFR2 in 2.16kg load were measured, and the ratio was computed. When this ratio is large, it is shown that the fluidity at the time of melting of a polymer is excellent, namely, workability is high.

[0194] After carrying out a temperature up from [glass-transition-temperature] ordinary temperature to 200 degrees C by part for 30-degree-C/, it held for 5 minutes, the temperature was lowered to -150 degrees C by part for 10-degree-C/, and it asked from the endoergic curve at the time of subsequently carrying out a temperature up by part for 10-degree-C/.

[0195] From the endoergic peak at the time of [degree-of-crystallinity] DSC measurement, the amount of heat of fusions per unit weight was calculated, and it \*(ed) and asked for this by amount of heat of fusions 70 cal/g of the crystal of polyethylene.

[0196] 2. After heat-treating physical-properties [consistency] 190 degree C of an ethylene system copolymer [B], high density polyethylene [C], and a propylene system polymer [D], and the strand after the MFR measurement in 2.16kg load for 1 hour and annealing them to a room temperature over 1 hour at 120 degrees C, it measured with the density gradient tube method.

[0197] The [alpha olefin content] 13 C-NMR spectrum determined.

It is determined by measuring the stress when extending the polymer which carried out [melting tension (MT)] fusion with constant speed. The granulation pellet of a polymer was made into the test portion, and it measured made in an Oriental energy machine factory and using MT measuring instrument on conditions with a part for /, a resin temperature [ of 190 degrees C ], and part [ for /] and diameter of 10-20mm nozzle in extrusion rate rolling-up rate of 15mm 2.09mmphi, and a nozzle die length of 8mm.

[0198] [MFR] ASTM Based on D-1238, MFR2 in 2.16kg load in 190 degrees C was measured.

[0199] [Softening temperature (Tm)] It asks for the endoergic curve of DSC and temperature of the maximum peak location is set to Tm. After measurement having put the sample in the aluminum pan, having carried out the temperature up to 200 degrees C by part for 10-degree-C/and holding it for 5 minutes at 200 degrees C, it was lowered to the room temperature by part for 20-degree-C/, and it asked for it from the endoergic curve at the time of

subsequently carrying out a temperature up by part for 10-degree-C/.

[0200]

[The example 1 of manufacture] Hexane 845ml was inserted in the autoclave made from SUS with an agitator with a capacity of 2l. which carried out the nitrogen purge enough at 23 degrees C. 155ml was inserted for 1-butene, having turned the agitator to this autoclave and cooling by iced water. Next, the autoclave was heated to 60 degree C of inside \*\*, and further, it pressurized with ethylene so that total pressure might be set to 8kg. In the place where the internal pressure of an autoclave became 8kg, 1.0 mM(s)/ml Deccan solution of triisobutylaluminum (TIBA) was pressed fit with 1.0ml nitrogen. Then, the toluene solution of 0.3ml of toluene solutions which contain methyl aluminoxane by aluminum conversion and contain 0.3 screw [ mM(s) and rac-dimethyl silylene-] [1- (2-methyl-4-phenyl-indenyl)] zirconium dichloride in the amount of 0.001mM(s) prepared beforehand was pressed fit in the autoclave with nitrogen, and the polymerization was started.

[0201] After that, for 30 minutes, the temperature control of the autoclave was carried out so that it might become 60 degree C of inside \*\*, and ethylene was directly supplied so that a pressure might be set to 8kg. After [ of polymerization initiation ] 30 minutes, methanol 5ml was inserted in the autoclave with the pump, the polymerization was suspended, and depressuring of the autoclave was carried out to atmospheric pressure. It poured stirring a 2l. acetone in a reaction solution.

[0202] When the polymer of the shape of a rubber ball containing the obtained solvent was dried by 600torr for 130 degrees C and 13 hours, ethylene and 47g of 1-butene copolymers which contain 1-butene 39 mmols were obtained.

[0203] The basic property of the obtained ethylene and 1-butene copolymer (A-1) is shown in Table 1. Moreover, ethylene and alpha olefin copolymer (A-2) - (A-7) were similarly obtained except having changed the class of monomer, and the charge.

[0204] The obtained ethylene and the alpha olefin copolymer (A-2) - (A-7) a basic property are shown in Table 1. Instead of the above-mentioned rac-dimethyl silylene-screw [1- (2-methyl-4-phenyl-indenyl)] zirconium dichloride, dimethyl silylene (2-methyl -4, 5-benzo -1 -indenyl) (2, 7-G t-butyl-9-fluorenyl) zirconium dichloride was used, the polymerization was carried out similarly, and ethylene and alpha olefin copolymer (A-8) - (A-10) were obtained.

[0205] The obtained ethylene and the alpha olefin copolymer (A-8) - (A-10) a property are shown in Table 2.

[0206]

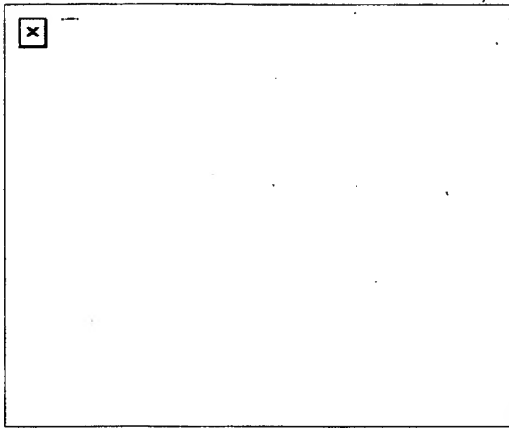
[Table 1]

表 1

| 共重合体                                | A-1         | A-2         | A-3         | A-4         | A-5          | A-6           | A-7           |
|-------------------------------------|-------------|-------------|-------------|-------------|--------------|---------------|---------------|
| $\alpha$ -オレフィン種<br>エチレン量(mol%)     | 1-ブテン<br>61 | 1-ブテン<br>70 | 1-ブテン<br>80 | 1-ブテン<br>36 | 1-ヘキセン<br>66 | 1-オクタテン<br>66 | 1-オクタテン<br>82 |
| 密度(g/cm <sup>3</sup> )              | 0.860       | 0.859       | 0.862       | 0.861       | 0.855        | 0.855         | 0.860         |
| [ $\eta$ ]                          | 2.3         | 2.4         | 2.4         | 2.2         | 2.2          | 2.1           | 2.3           |
| Mw/Mn                               | 2.4         | 2.2         | 2.2         | 2.5         | 2.3          | 2.3           | 2.3           |
| MFR <sub>10</sub> /MFR <sub>2</sub> | 10.2        | 13.5        | 12.2        | 10.5        | 9.9          | 9.6           | 8.9           |
| Tg (°C)                             | -64         | -66         | -83         | -59         | -68          | -69           | -67           |
| 結晶化度(%)                             | 0           | 0           | 10          | 0           | 0            | 0             | 9             |
| Ta $\beta$ /Taa                     | <0.01       | <0.01       | <0.01       | <0.01       | <0.01        | <0.01         | <0.01         |
| B 値                                 | 1.11        | 1.04        | 1.03        | 1.00        | 1.07         | 1.08          | 1.04          |

[0207]

[Table 2]



<BR>

[0208]

[Table 3]

表 3

| 共重合体                   | B-1   | B-2   | C-1   | B-3   | D     |
|------------------------|-------|-------|-------|-------|-------|
| コモノ種類                  | 1-ブテン | 1-ブテン | プロピレン | —     | —     |
| コモノ量(mol%)             | 4.8   | 1.4   | 0.6   | —     | —     |
| 比重(g/cm <sup>3</sup> ) | 0.908 | 0.938 | 0.952 | 0.925 | 0.910 |
| MFR (g/10分)            | 1.7   | 4.5   | 1.6   | 2.1   | 22    |
| MT (g)                 | 1.2   | 0.4   | 1.2   | 4.1   |       |
| 2.2xMFR-O. **          | 1.4   | 0.6   | 1.5   | 1.2   |       |
| Tm (°C)                | 94    | 118   | 130   | 109   |       |
| 400x d-250             | 113   | 125   | 131   | 120   |       |

B-3はエチレン単独重合体、Dはプロピレン単独重合体

[0209]

[Example 1] ethylene and 60 % of the weight (A-1) of 1-butene copolymers, and 40 % of the weight (B-2) of ethylene system polymers -- a lab PURASUTO mill (Oriental energy machine company make) -- using -- 60rpm and 200 degrees C -- for 5 minutes -- kneading -- pelletizing -- ethylene -- the 1-butene copolymer / ethylene system polymer pre blend pellet was obtained. the obtained ethylene -- about the 1-butene copolymer / ethylene system polymer pre blend pellet, the pellet blocking trial was performed and blocking nature was evaluated.

[0210] A result is shown in Table 4.

The pellet was put into the bag made from [pellet blocking trial] polyethylene, and within the oven set as 35 degrees C, after leaving it under 100g[ /cm ] 2 load for 72 hours, the blocking condition of an ejection pellet was evaluated as follows.

[0211]

O : -- almost -- blocking-less O: -- x: pellet which can be pushed and unfolded by \*\*:hand which can be unfolded easily by hand welds, and it becomes bail-like [0212]

[Examples 2-8] By combination as shown in Table 4, the pellet blocking trial was performed like the example 1. Pellet blocking could not take place easily and all of workability were good.

[0213] A result is shown in Table 4.

[0214]

[Table 4]

表 4

|        | 実施例1 | 実施例2 | 実施例3 | 実施例4 | 実施例5 | 実施例6 | 実施例7 | 実施例8 |
|--------|------|------|------|------|------|------|------|------|
| A-1    | 60   |      |      |      |      |      |      | 60   |
| A-2    |      | 60   |      |      |      |      |      |      |
| A-5    |      |      | 60   |      |      |      |      |      |
| A-6    |      |      |      | 60   |      |      |      |      |
| A-8    |      |      |      |      | 60   |      |      |      |
| A-9    |      |      |      |      |      | 60   |      |      |
| A-10   |      |      |      |      |      |      | 60   |      |
| B-1    | 40   | 40   | 40   | 40   | 40   |      |      |      |
| B-2    |      |      |      |      |      | 40   | 40   |      |
| C-3    |      |      |      |      |      |      |      | 40   |
| ブロッキング | ◎    | ◎    | ○    | ○    | ◎    | ○    | ○    | ◎    |

組成は重量%

[0215]

[The examples 1-7 of a comparison] By combination as shown in Table 5, the pellet blocking trial was performed like the example 1. Pellet blocking occurred and all had bad workability.

[0216] A result is shown in Table 5.

[0217]

[Table 5]

表 5

|        | 比較例1 | 比較例2 | 比較例3 | 比較例4 | 比較例5 | 比較例6 | 比較例7 |
|--------|------|------|------|------|------|------|------|
| A-1    | 100  |      |      |      |      |      |      |
| A-2    |      | 100  |      |      |      |      |      |
| A-5    |      |      | 100  |      |      |      |      |
| A-6    |      |      |      | 100  |      |      |      |
| A-8    |      |      |      |      | 100  |      |      |
| A-9    |      |      |      |      |      | 100  |      |
| A-10   |      |      |      |      |      |      | 100  |
| ブロッキング | ×    | ×    | ×    | ×    | ×    | ×    | ×    |

組成は重量%

[0218]

[Example 9] ethylene and 60 % of the weight (A-1) of 1-butene copolymers, and 40 % of the weight (B-2) of ethylene system polymers -- a lab PURASUTO mill -- using -- 60rpm and 200 degrees C -- for 5 minutes -- kneading -- pelletizing -- ethylene -- the -1-butene copolymer / ethylene system polymer pre blend pellet was obtained. subsequently, the obtained ethylene -- gay (polypropylene C) 70% of the weight, as a stabilizer, calcium stearate was added 0.1% of the weight, IRUGA NOx 168 was added for IRUGA NOx 1010 0.1% of the weight 0.1% of the weight, using the lab PURASUTO mill, 150 rpm, it kneaded for 5 minutes on a -1-butene copolymer / 30 % of the weight of ethylene system polymer pre blend pellets, and 200 degrees C was pelletized on them. Press forming of the obtained pellet was carried out at 230 degrees C, and fracture point elongation, flexural strength, impact strength-proof, and viscoelasticity were measured by the evaluation approach shown below.

[0219] A result is shown in Table 6.

[Fracture point elongation (EB)] ASTM D Based on 638, it measured at the room temperature.

[Flexural strength (FM)] ASTM D Based on 790, it measured using the test piece with a thickness of 2mm which carried out injection molding on predetermined conditions under 32mm, and 5m conditions for /in bending rate between spans.

[Impact strength-proof (IZ)] ASTM D Based on 256, it measured at -30 degrees C using the test piece (back notch) with a thickness of 3mm.



The temperature dependence of the dynamic viscoelasticity to  $-80-50$  degrees C was measured on the frequency of 62.5 rads/sec using RDSII by [viscoelasticity] REOMETO Rix Corp., and it judged whether the peak of the damping factor (tan delta) resulting from the glass transition temperature of a polypropylene system polymer [D] and the peak of the damping factor (tan delta) resulting from the glass transition temperature of ethylene and an alpha olefin copolymer constituent have dissociated, or it would have united.

[0220]

[Example 10] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-2) with which the contents of an alpha olefin differ.

[0221] A result is shown in Table 6.

[0222]

[Example 11] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-5) with which an alpha olefin kind differs from a content.

[0223] A result is shown in Table 6.

[0224]

[Example 12] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-6) with which an alpha olefin kind differs from a content.

[0225] A result is shown in Table 6.

[0226]

[Example 13] Instead of the ethylene system polymer (B-2), the pellet was fabricated and evaluated like the example 9 except having used the ethylene system polymer (B-1).

[0227] A result is shown in Table 6.

[0228]

[The example 8 of a comparison] The pellet was fabricated and evaluated like the example 9 except the contents of an alpha olefin differing, namely, having used the ethylene and the alpha olefin copolymer (A-3) which separated from the range of this invention.

[0229] A result is shown in Table 6. The balance of impact strength and flexural strength was bad, and impact strength was low comparatively [ with low flexural strength ].

[0230]

[The example 9 of a comparison] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-4) with which the contents of an alpha olefin differ.

[0231] A result is shown in Table 6. The balance of impact strength and flexural strength was bad, and impact strength was low comparatively [ with low flexural strength ].

[0232]

[The example 10 of a comparison] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-7) with which an alpha olefin kind differs from a content.

[0233] A result is shown in Table 6. The balance of impact strength and flexural strength was bad, and impact strength was low comparatively [ with low flexural strength ].

[0234]

[Table 6]

表 6

|                           | 実施例9 | 実施例10 | 実施例11 | 実施例12 | 実施例13 | 比較例8 | 比較例9 | 比較例10 |
|---------------------------|------|-------|-------|-------|-------|------|------|-------|
| エチレン・ $\alpha$ -オレフィン共重合体 |      |       |       |       |       |      |      |       |
| A-1                       | 18   |       |       |       | 18    |      |      |       |
| A-2                       |      | 18    |       |       |       |      |      |       |
| A-3                       |      |       |       |       |       | 18   |      |       |
| A-4                       |      |       |       |       |       |      | 18   |       |
| A-5                       |      |       | 18    |       |       |      |      |       |
| A-6                       |      |       |       | 18    |       |      |      |       |
| A-7                       |      |       |       |       |       |      |      | 18    |

|               |      |      |      |      |      |      |     |      |
|---------------|------|------|------|------|------|------|-----|------|
| エチレン系共重合体 B-1 | 12   | 12   | 12   | 12   | 12   | 12   | 12  | 12   |
| B-2           | 12   | 12   | 12   | 12   | 12   | 12   | 12  | 12   |
| ポリプロピレン D     | 70   | 70   | 70   | 70   | 70   | 70   | 70  | 70   |
| E B (%)       | 250  | 370  | 410  | 420  | 300  | 180  | 650 | 270  |
| FM (J/m)      | 1060 | 1180 | 1050 | 1030 | 1020 | 1290 | 820 | 1270 |
| I Z (J/m)     | 41   | 30   | 38   | 39   | 38   | 17   | 17  | 18   |
| tan δ ビーク     | 分離   | 分離   | 分離   | 分離   | 分離   | 分離   | 融合  | 分離   |

組成は重量%

[0235]

[Example 14] In the example 9, the pellet was fabricated and evaluated like the example 9 except having used high density polyethylene (C-1) instead of the ethylene system polymer (B-2).

[0236] A result is shown in Table 7.

[0237]

[The example 11 of a comparison] In the example 9, the pellet was fabricated and evaluated like the example 9 except having used low density polyethylene (B-3) instead of the ethylene system polymer (B-2).

[0238] A result is shown in Table 7. Fracture point elongation and impact strength were not improved.

[0239]

[Example 15] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-8) with which the contents of an alpha olefin differ.

[0240] A result is shown in Table 7.

[0241]

[Example 16] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-9) with which an alpha olefin kind differs from a content.

[0242] A result is shown in Table 7.

[0243]

[Example 17] The pellet was fabricated and evaluated like the example 9 except having used the ethylene and the alpha olefin copolymer (A-10) with which an alpha olefin kind differs from a content.

[0244] A result is shown in Table 7.

[0245]

[The example 12 of a comparison] Except having considered as ethylene and 30 % of the weight (A-1) of alpha olefin copolymers, and propylene system (polymer D) 70 % of the weight, and having not added an ethylene system copolymer or high density polyethylene, the constituent was manufactured like the example 9 and shaping evaluation was carried out.

[0246] A result is shown in Table 7. The balance of rigidity and low-temperature impact resistance was inferior to the example 14. Moreover, the balance of rigidity and fracture point elongation was inferior to the example 1.

[0247]

[Table 7]

表 7

|                  | 実施例14 | 比較例11 | 実施例15 | 実施例16 | 実施例17 | 比較例12 |
|------------------|-------|-------|-------|-------|-------|-------|
| エチレン-α-オレフィン共重合体 |       |       |       |       |       |       |
| A-1              | 18    | 18    |       |       |       | 30    |
| A-8              |       |       | 18    |       |       |       |
| A-9              |       |       |       | 18    |       |       |
| A-10             |       |       |       |       | 18    |       |
| エチレン系共重合体        |       |       |       |       |       |       |
| B-2              |       |       | 12    | 12    | 12    |       |
| B-3              |       | 12    |       |       |       |       |
| B-1              |       |       |       |       |       |       |

|                            |          |      |      |      |      |     |
|----------------------------|----------|------|------|------|------|-----|
| 高純度ポリエチレン C-1<br>ポリプロピレン D | 12<br>70 | 70   | 70   | 70   | 70   | 70  |
| E B (%)                    | 50       | 80   | 210  | 380  | 390  | 250 |
| F M (J/m)                  | 1080     | 1070 | 1070 | 1050 | 1040 | 950 |
| I Z (J/m)                  | 47       | 40   | 37   | 36   | 37   | 40  |
| tan $\delta$ ビーク           | 分離       | 分離   | 分離   | 分離   | 分離   | 分離  |

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[Translation done.]